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Final Report - SRNL Agreement #AC51296V

J.P. Bradley, Z. R. Dai, G. A. Graham, N. E. Teslich

August 29, 2007

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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SEM, FIB & TEM Studies of CZT Samples

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UCRL-XXX-XXXX

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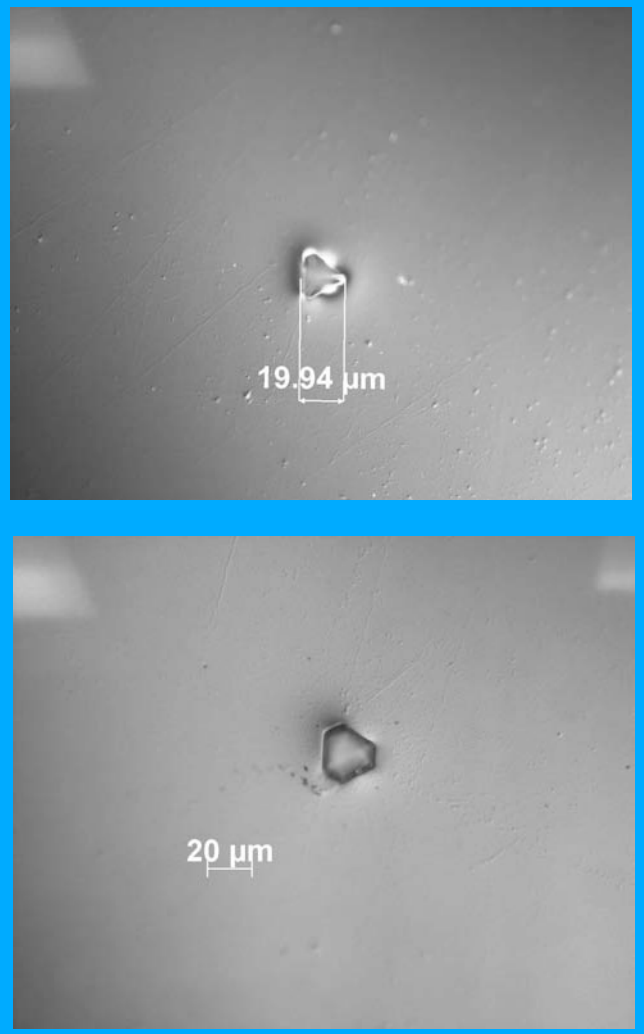
Aims of Studies

- To characterize the surfaces of samples 3-7-8-3 and 4-1-3 using SEM, FIB and TEM techniques.
- Identify raised surface features.
- Prepare FIB-TEM lift-out sections from identified raised surfaces
- Perform detailed TEM characterization of FIB Sections. Focusing on the composition and crystallinity of the phases within the sections, including impurities.



Reflected light optical images of features identified on the side A of sample 3-7-8-3

1. SEM Observations

i. 3-7-8-3 Side A (Te-rich face)

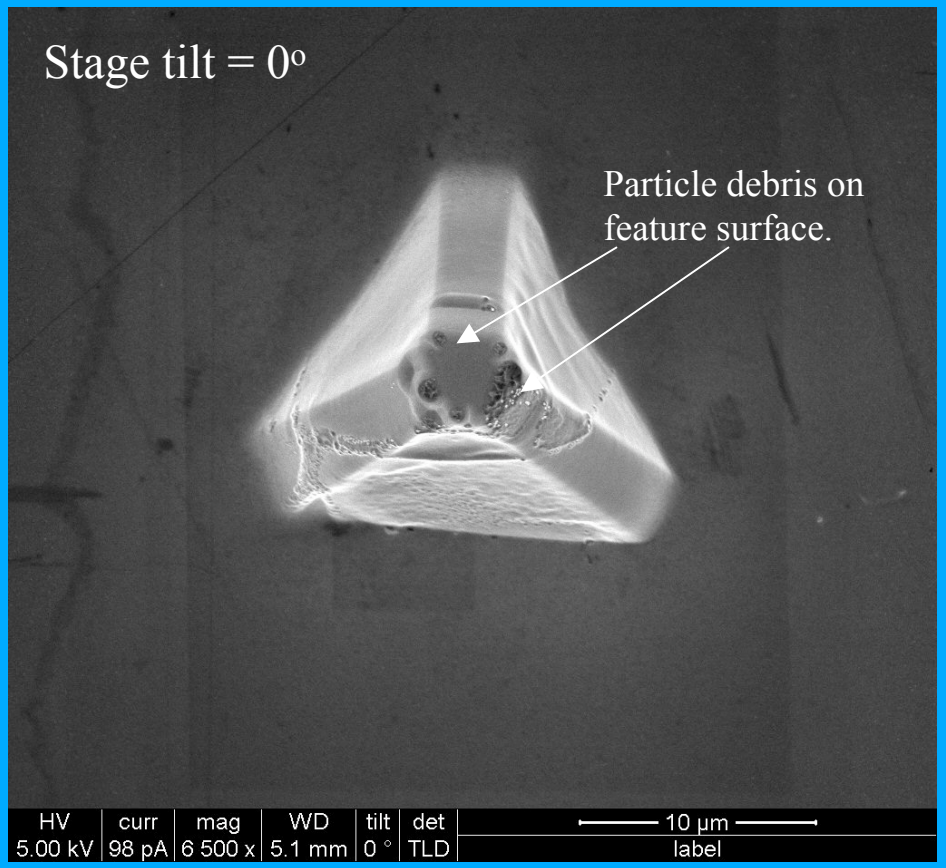
ii. 3-7-8-3 Side B (Cd-rich face)

iii. 4-1-3 Side A (Te-rich face)

iv. 4-1-3 Side B (Cd-rich face)

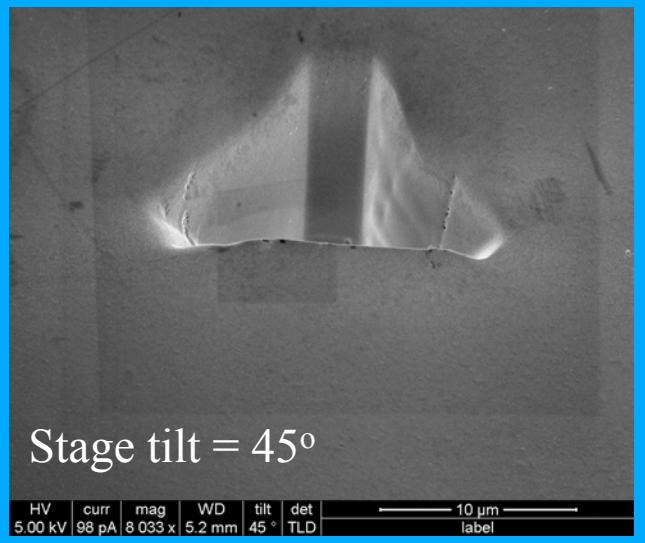
v. Additional Imaging Techniques

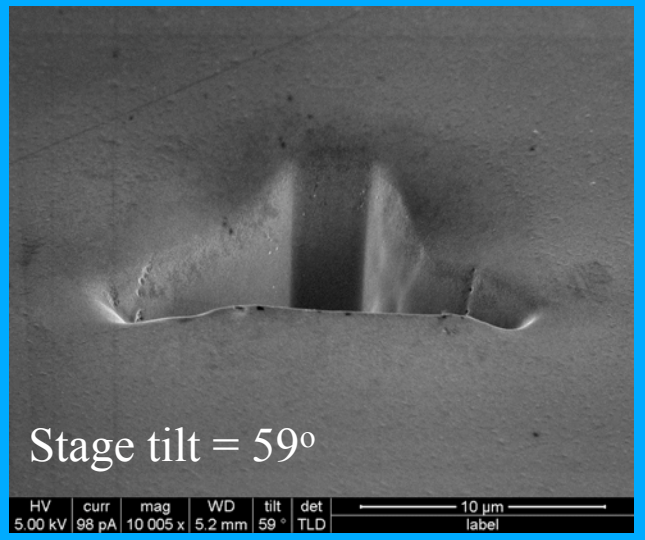
i. 3-7-8-3 Side A (Te-rich face)



Secondary electron image of "pyramid" surface feature.

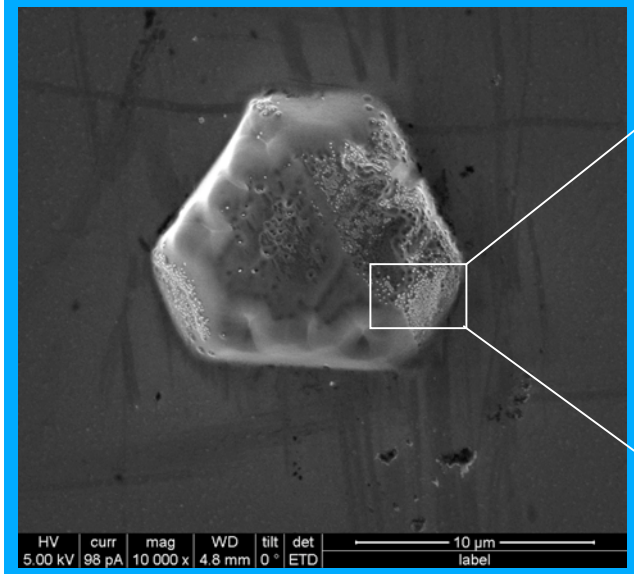
(All images acquired at 5 kV and in secondary electron mode using an FEI Nova 600 Nanolab Dualbeam FIB-FESEM)

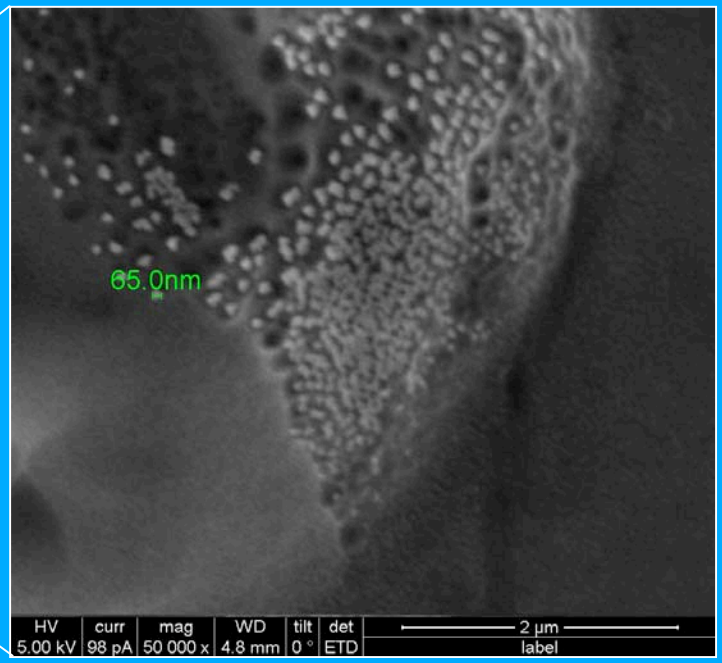




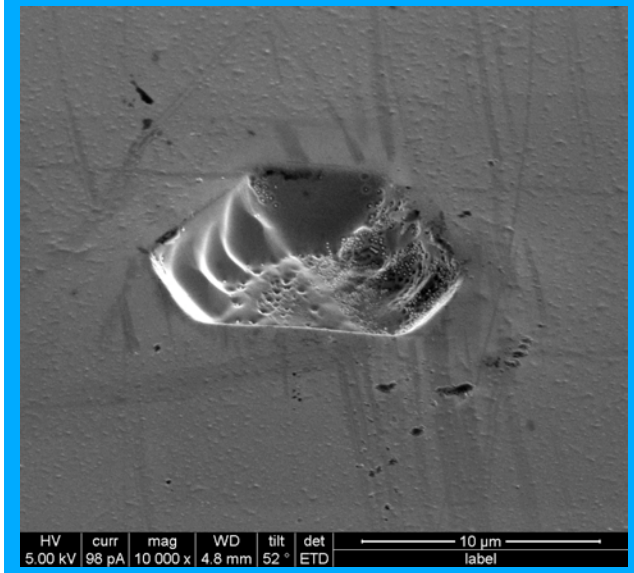
Stage tilts at 45° and 59° reveal that the pyramid feature is a depression rather than a raised feature as indicated by the optical images.

SEM & EDS Analysis of Surface Feature

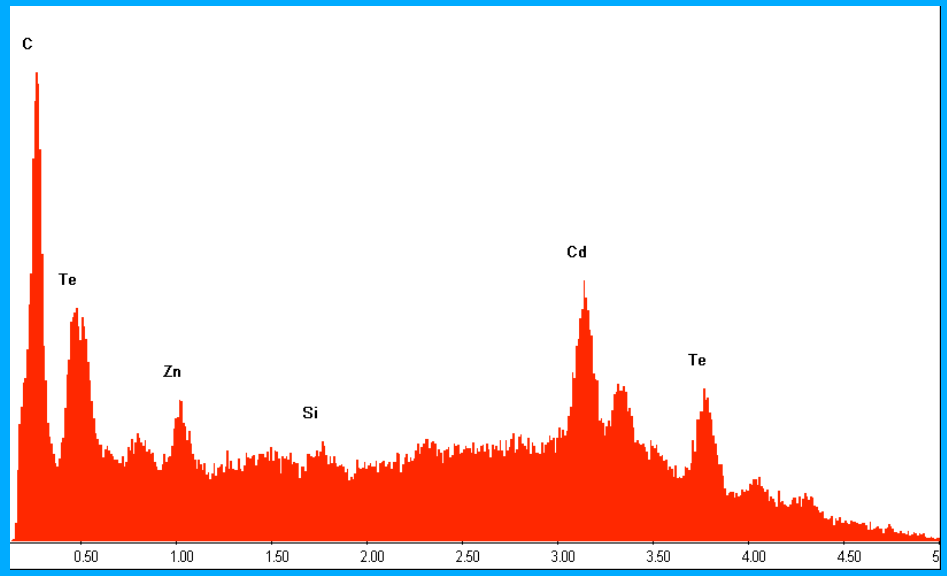




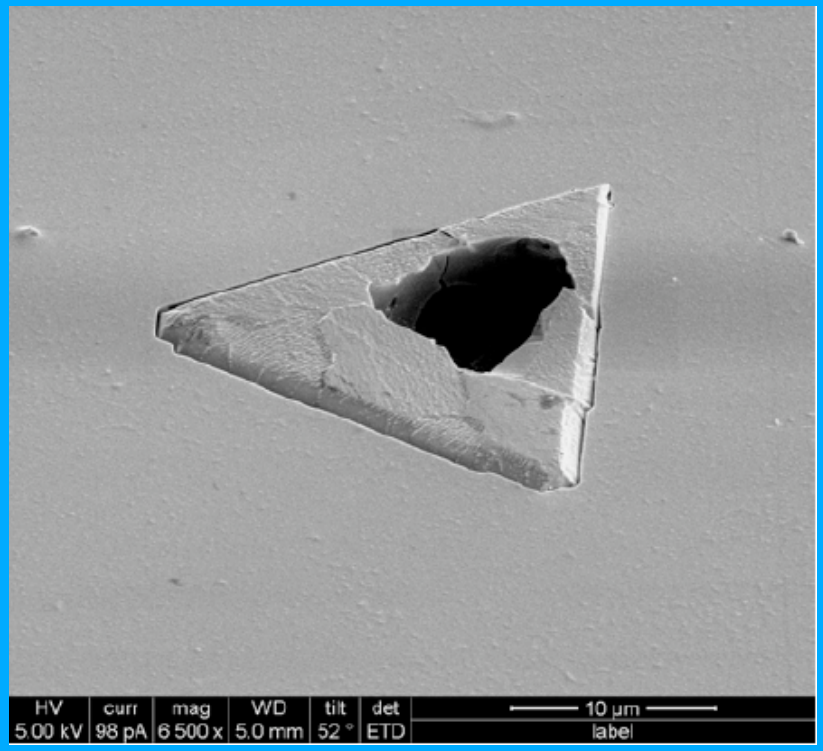
The "residue" particles are on the order of 65 nm in size. The particles are extremely beam sensitive and can be eroded away during image acquisition.

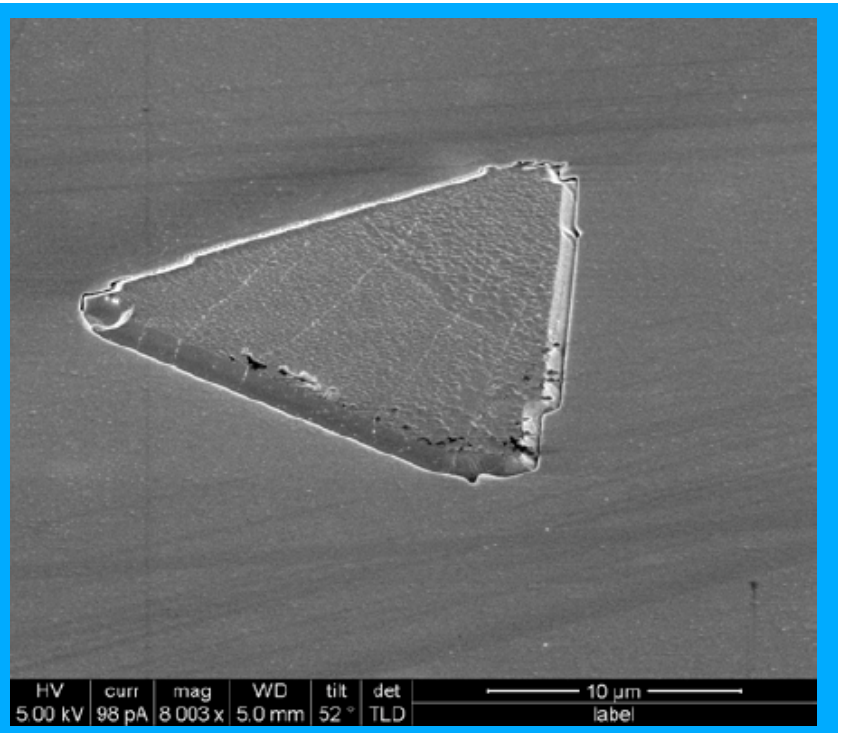


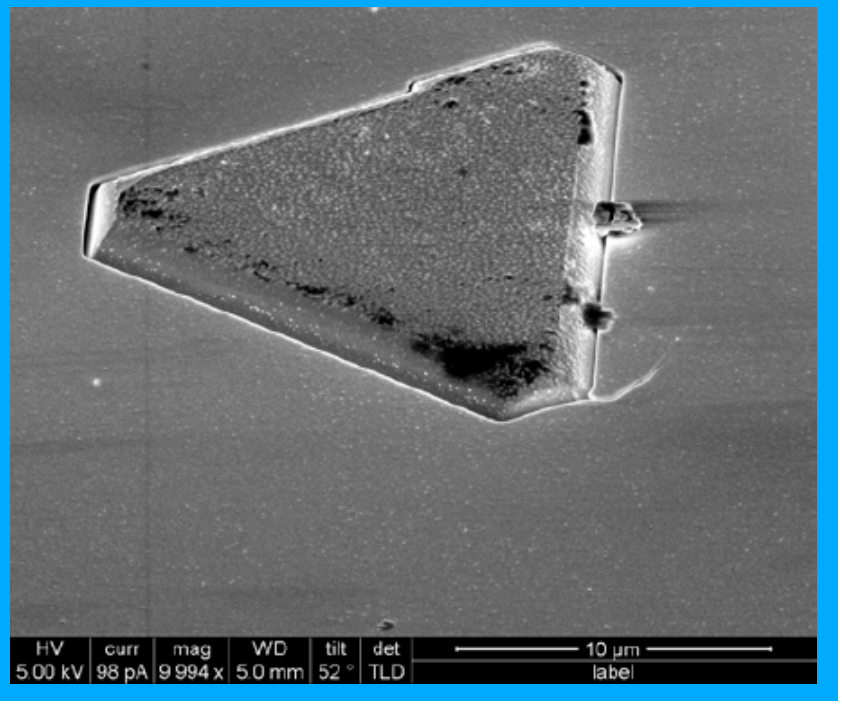
- Feature is a depression on the surface.



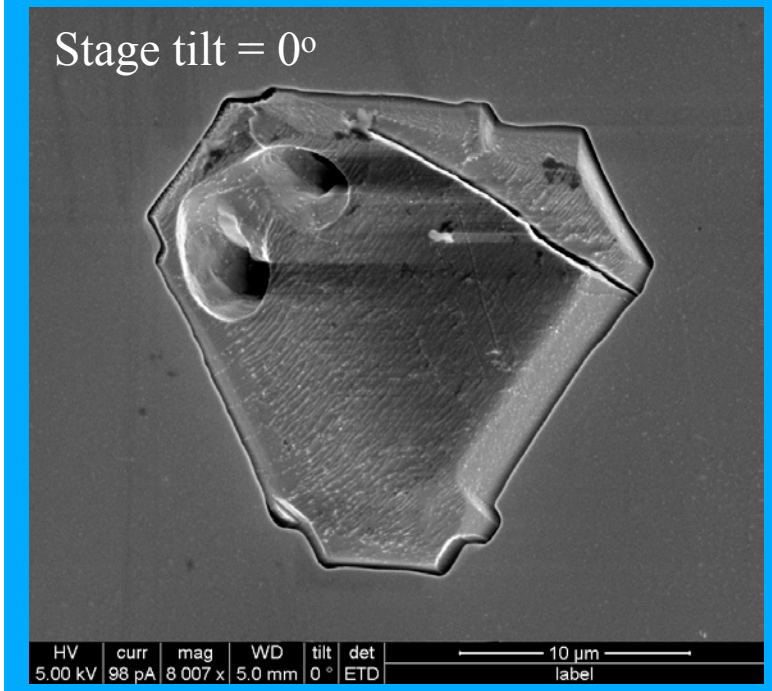
3-7-8-3 Side A (Te-rich face)
Raised Surface Features

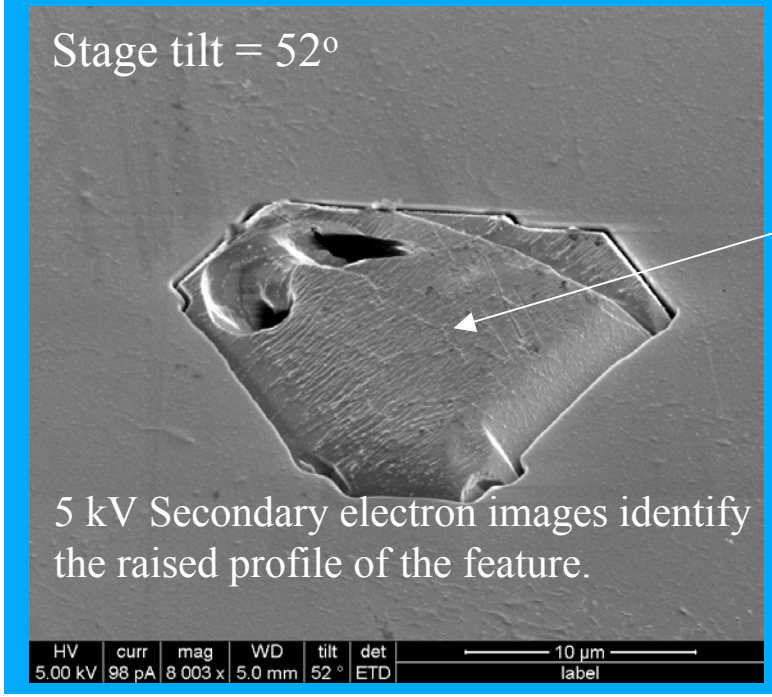






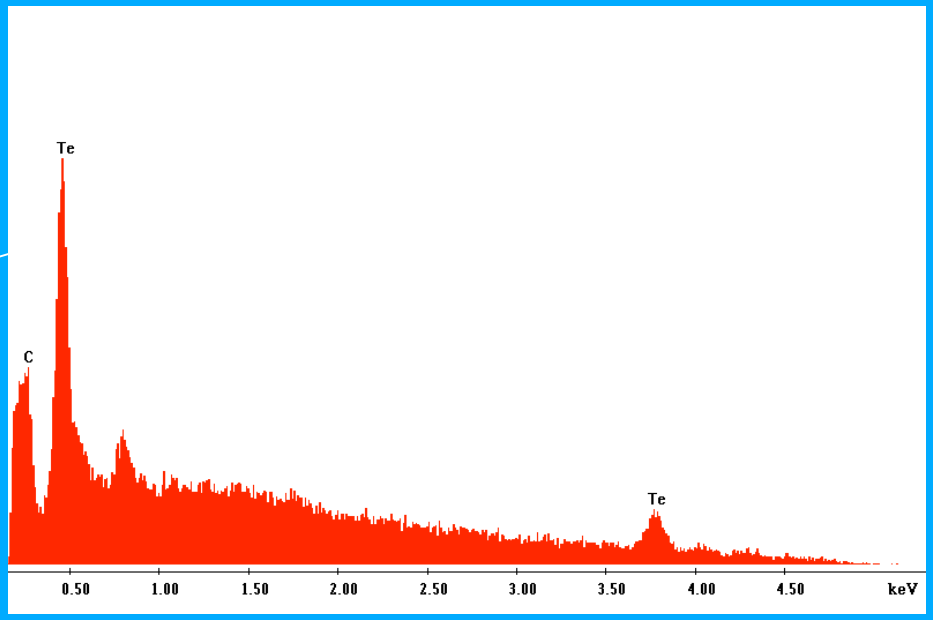
(All images acquired at 5 kV and in secondary electron mode using an FEI Nova 600 Nanolab Dualbeam FIB-FESEM)





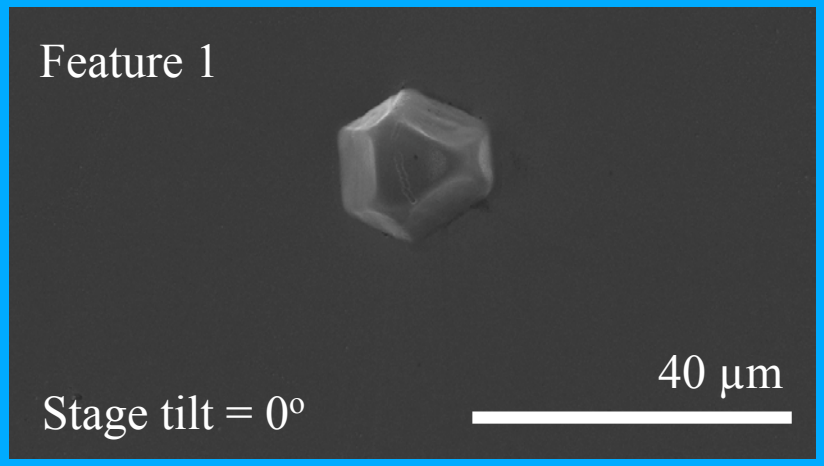
SEM & EDS Analysis of Raised Surface Feature

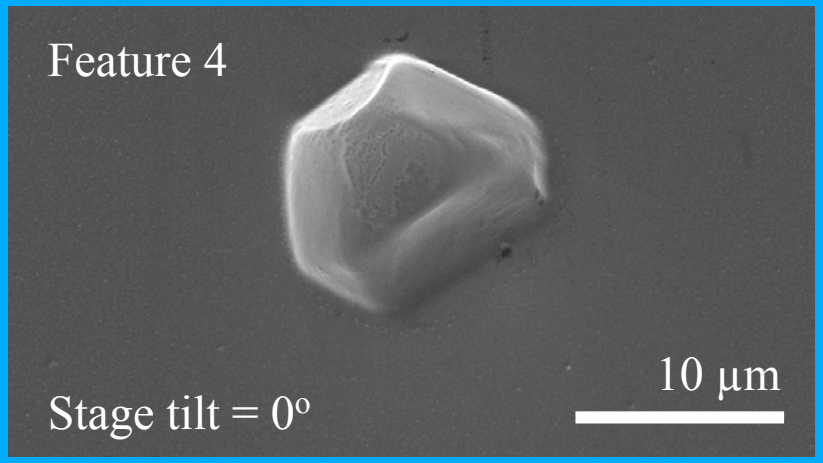
- Continued SEM survey of the side A surface identified the feature on the left hand-side which still contains a large amount of material which has yet to be eroded away. Unlike the previous features the one identified here is raised above the ambient surface plane.

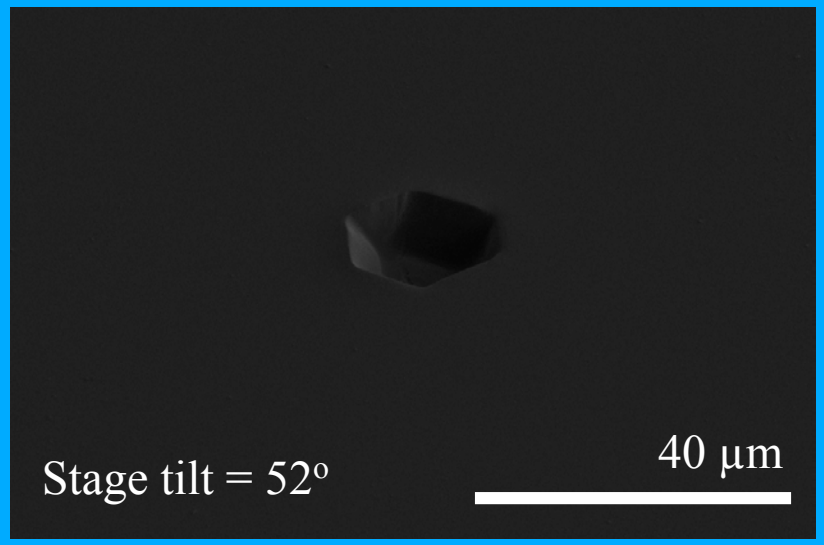


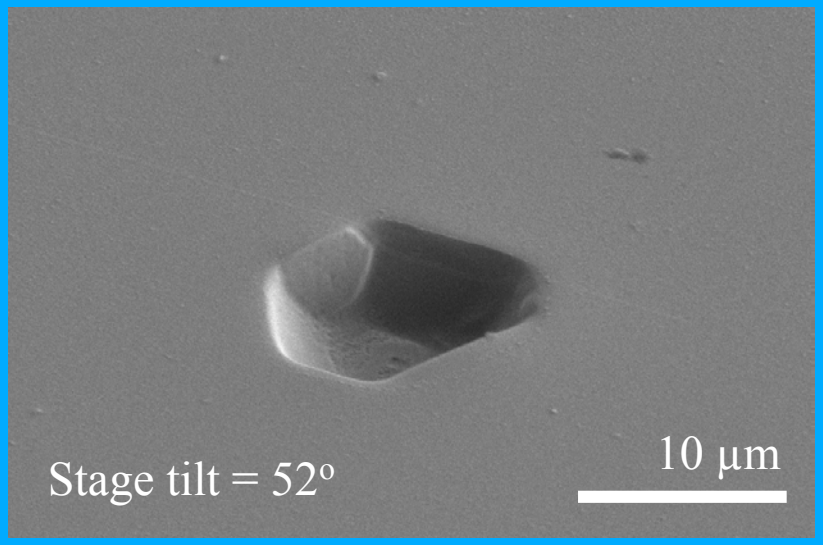
5 kV EDS spectrum acquire for the material. It appears to be sole composed of Te

ii. 3-7-8-3 Side B (Cd-rich face)



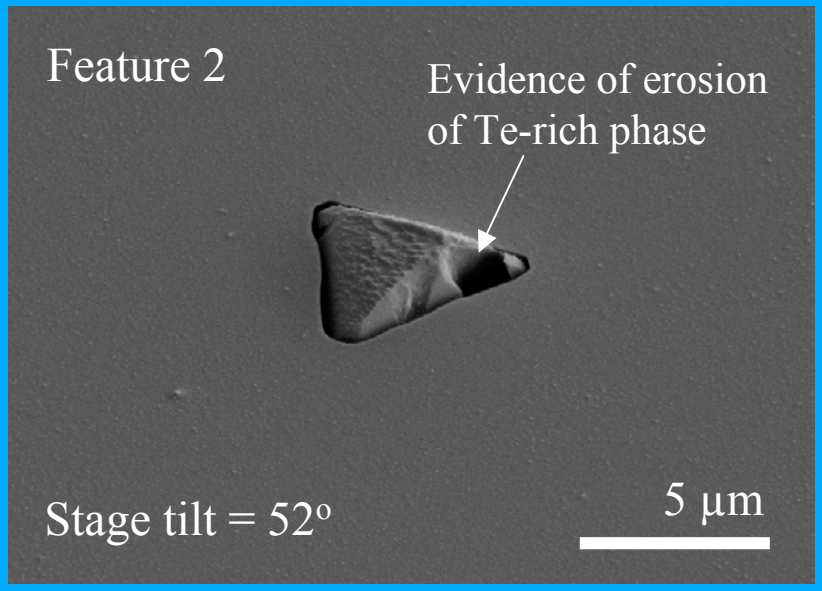


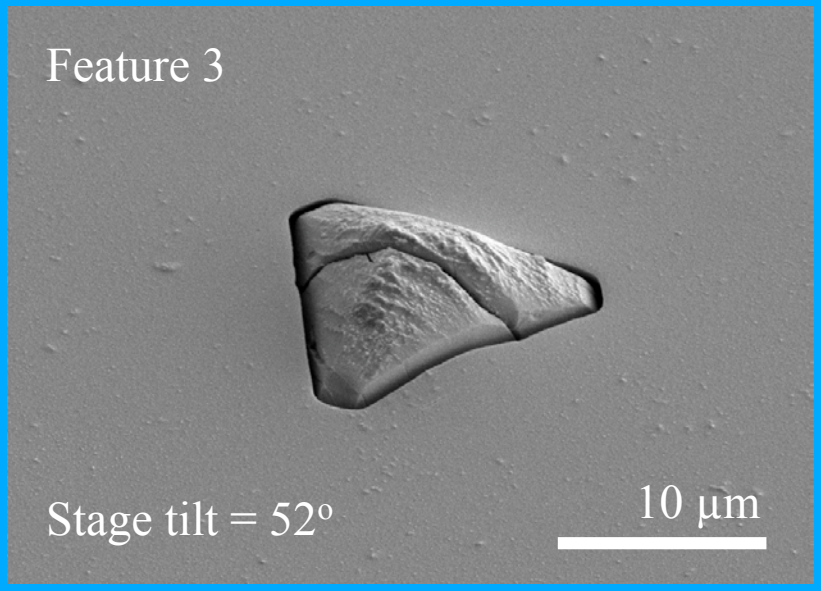


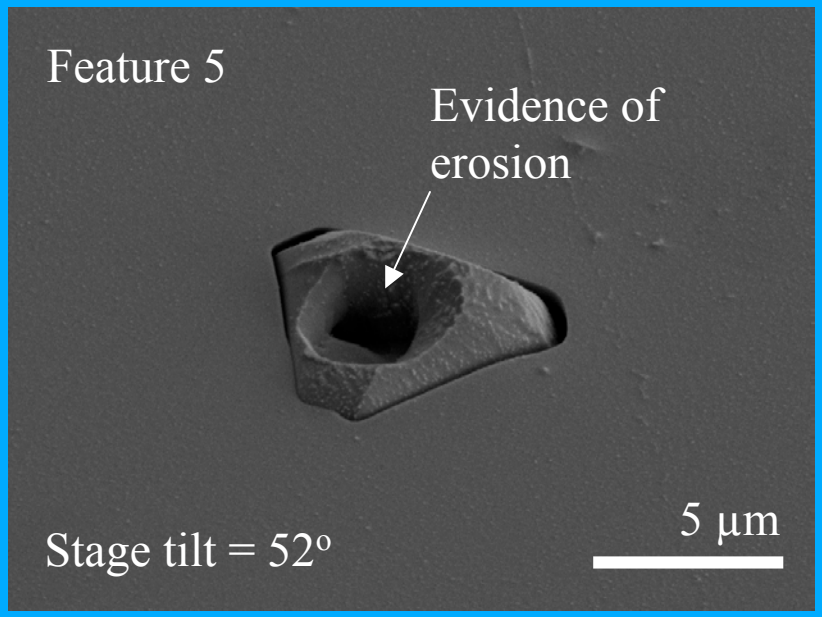


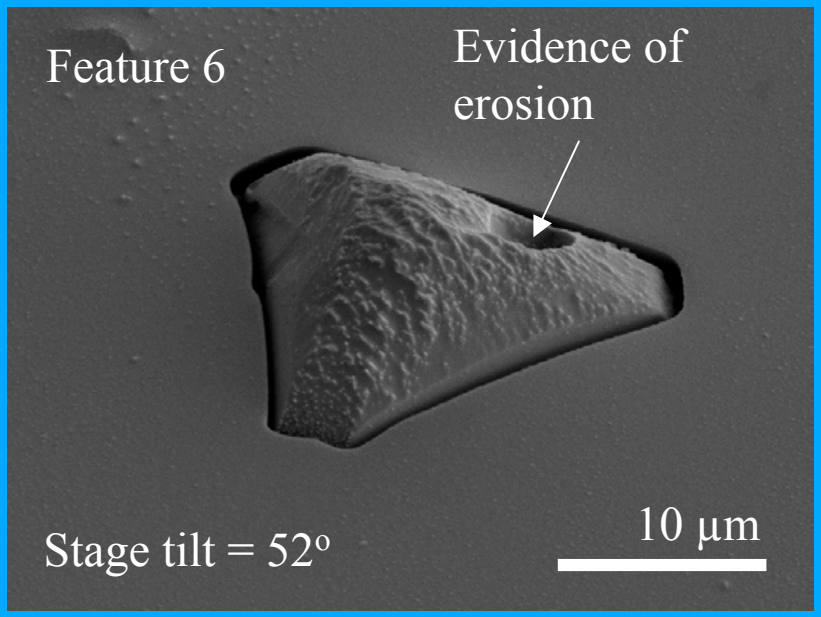
Features 1 & 4 revealed as surface depressions rather than raised features as possibly indicated from IR microscopy. Features do not appear to have retained evidence of particulate residues previously identified in similar feature on Side A.

(All images acquired at 5 kV and in secondary electron mode using an FEI Nova 600 Dualbeam FIB-FESEM)





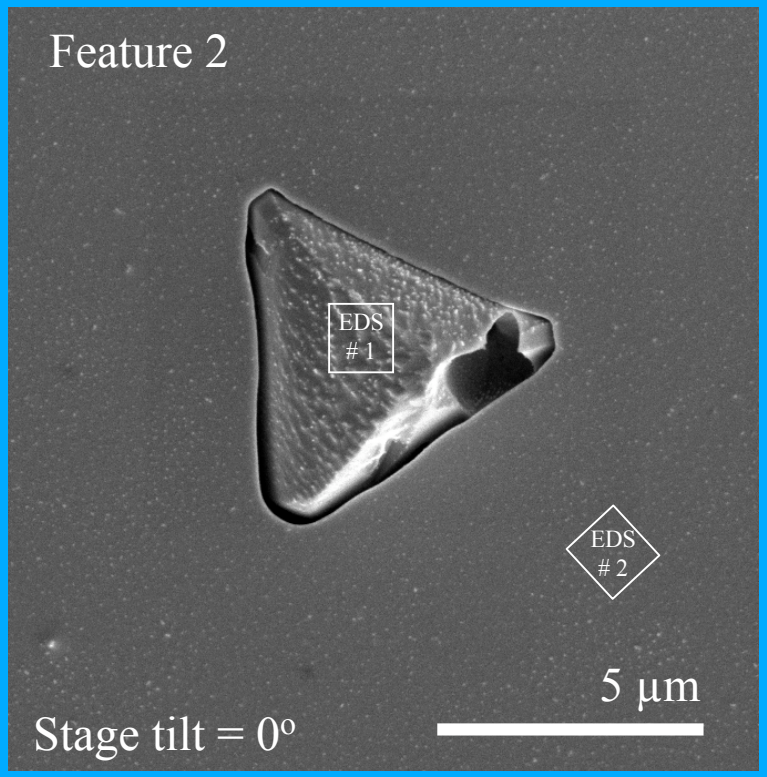




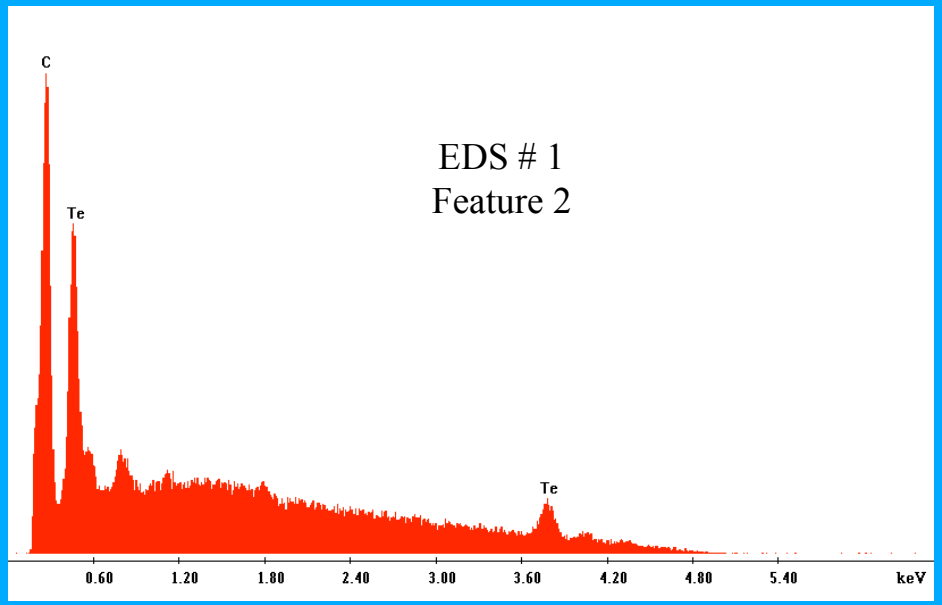
5 kV secondary electron images of features 2,3,5 and 6 which are raised above the ambient surface plane of the Cd-rich face.

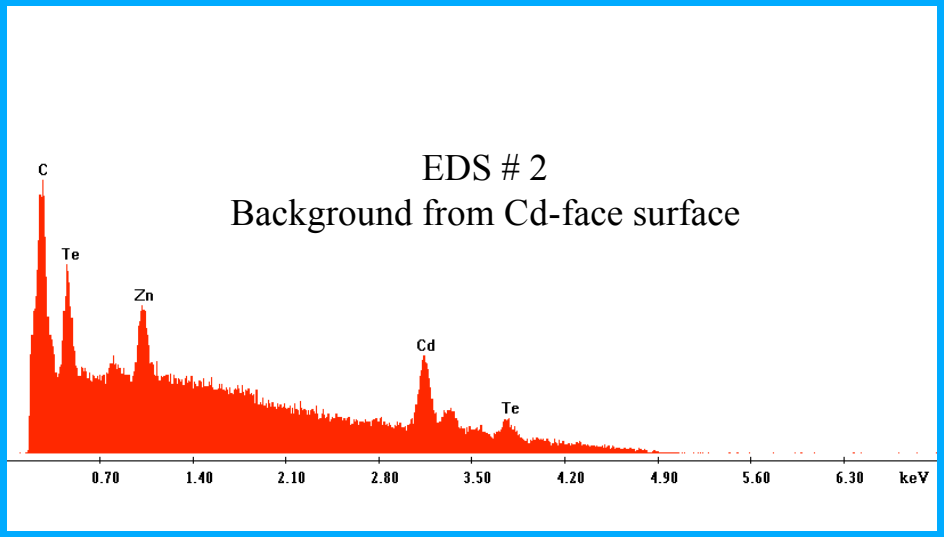
(All images acquired using an FEI Nova 600 Dualbeam FIB-FESEM)

EDS Analysis Feature 2 on Sample 3-7-8-3 Side B



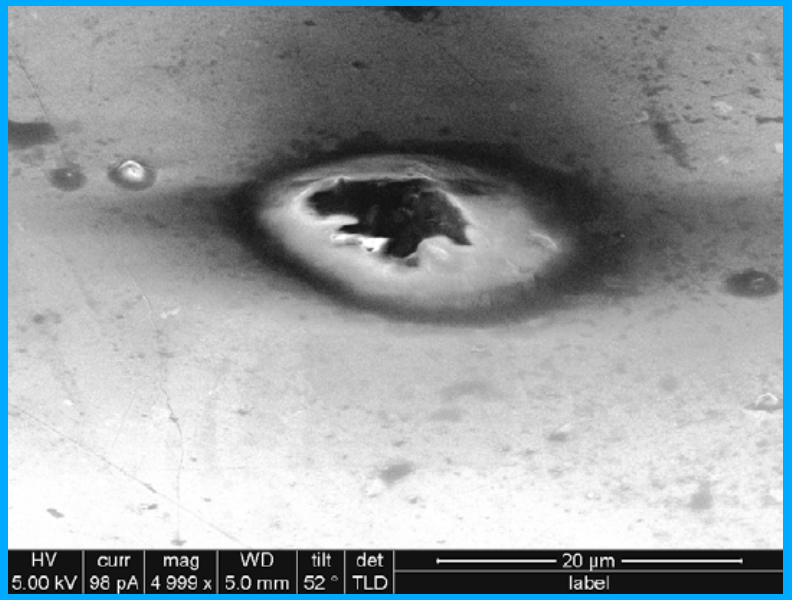
5 kV secondary electron image of raised feature on Cd-rich face

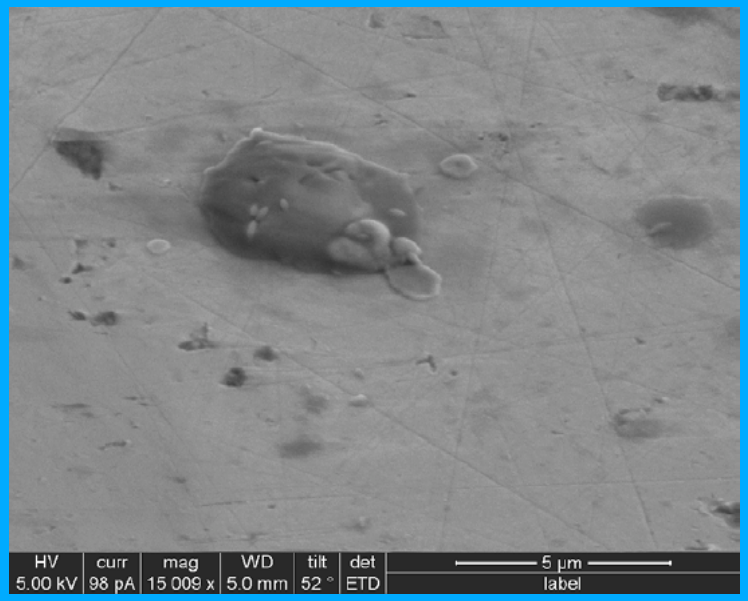




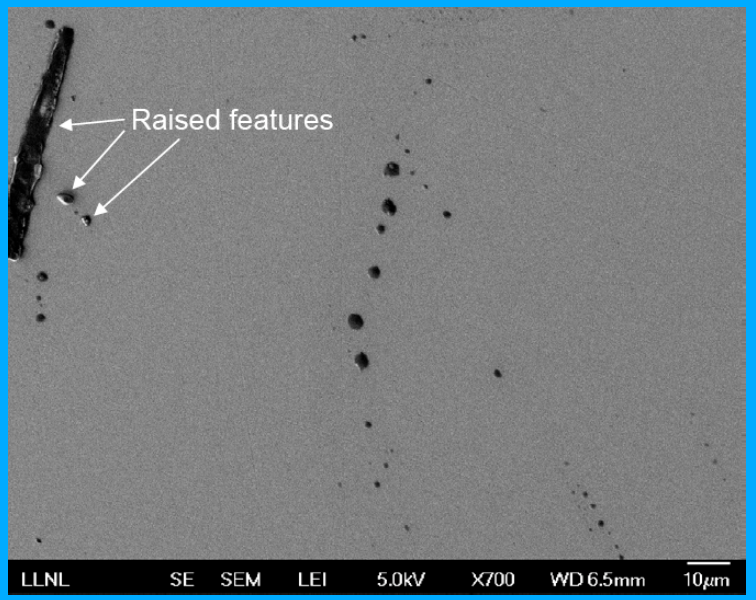
(Image and spectra acquired using an FEI Nova 600 Dualbeam FIB-FESEM)

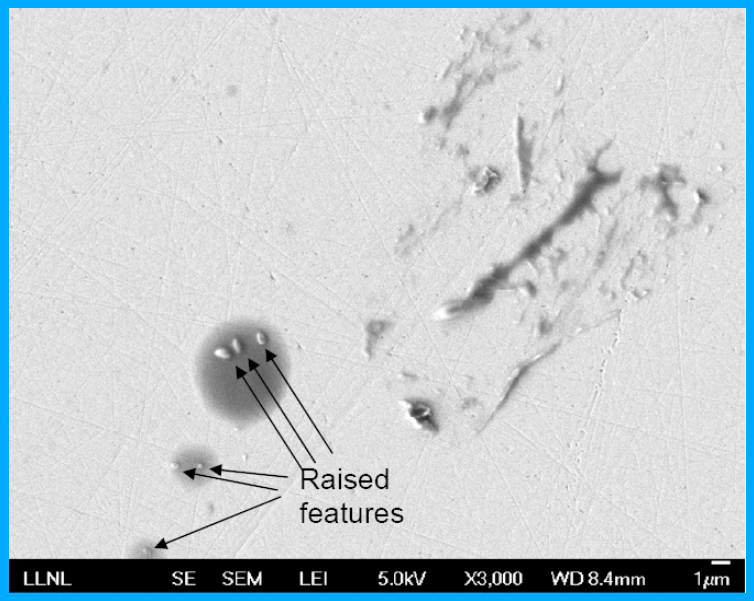
iii. 4-1-3 Side A (Te-rich face)





iv. 4-1-3 Side B (Cd-rich face)

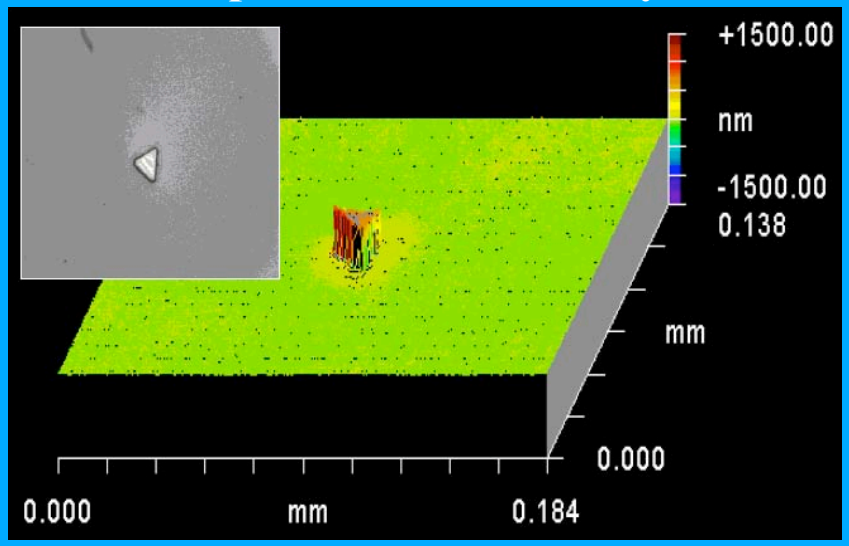


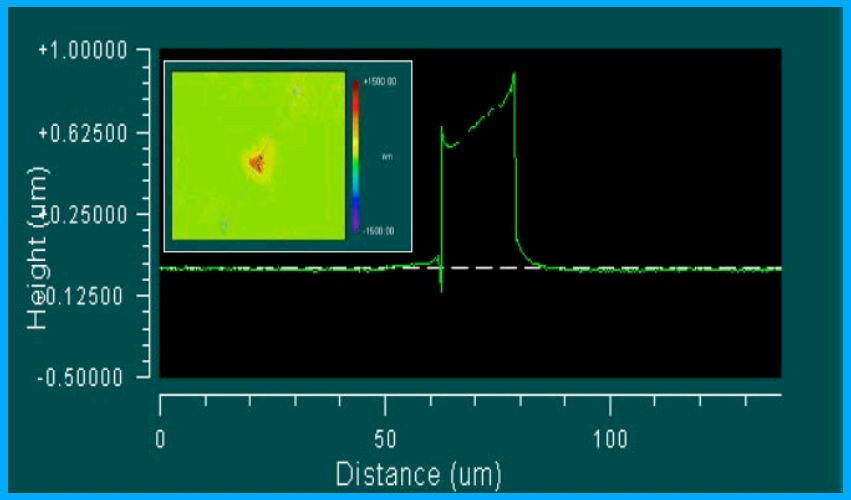


Raised surface structures do not have the clearly defined morphology seen on 3-7-8-3

v. Additional Imaging Techniques

Optical Interferometry

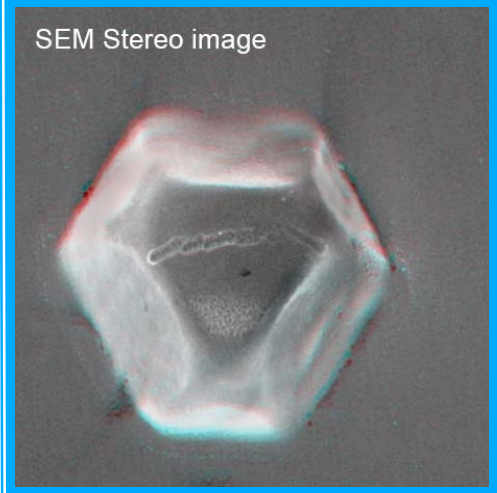


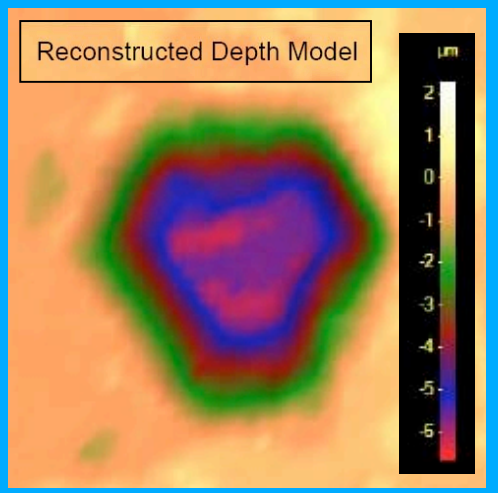


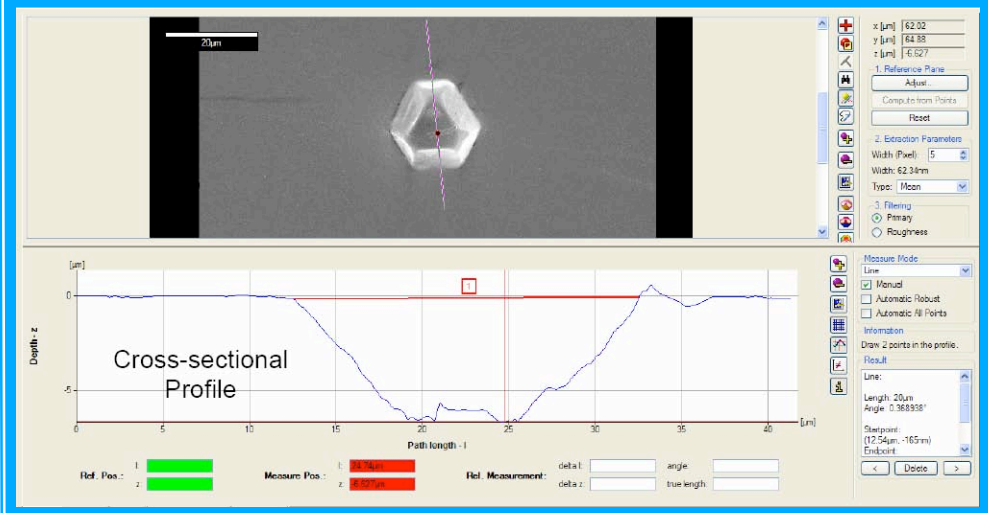
- Side A (Te-rich face) was imaged using a ZYGO 3D optical profiler.
- Manual scan identified both raised and depressed surface features.

3D Surface Imaging using SEM Data

From stereo anaglyphs it is possible to generate reconstructed colored-coded depth models and vertical cross-sectional profiles of features using Alicona MeX imaging processing software.







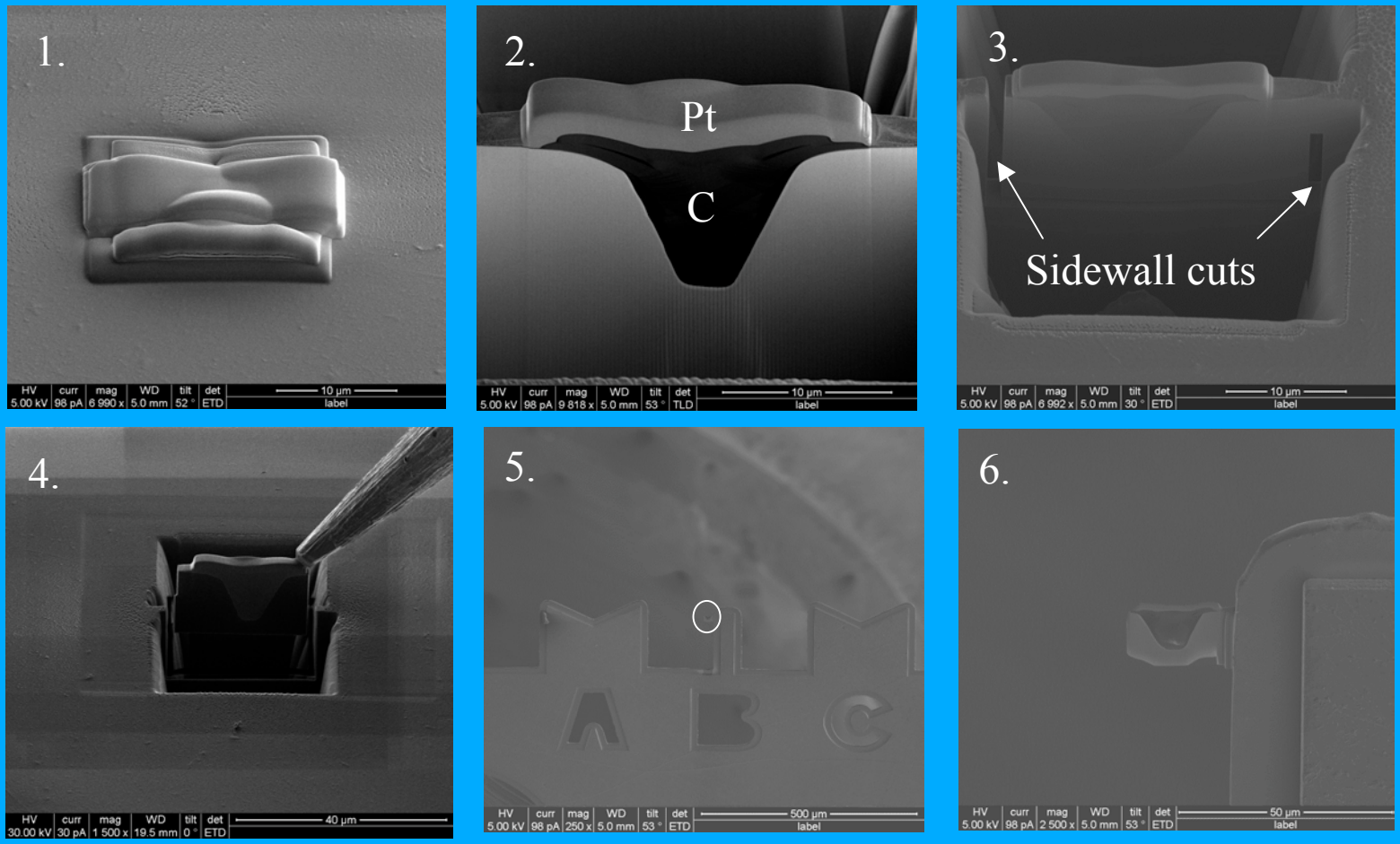
(SEM reconstruction data courtesy of A.T. Kearsley, NHM)

2. FIB-TEM Sample Preparation

i. FIB-TEM Section From 3-7-8-3 Side A (Te-rich face)

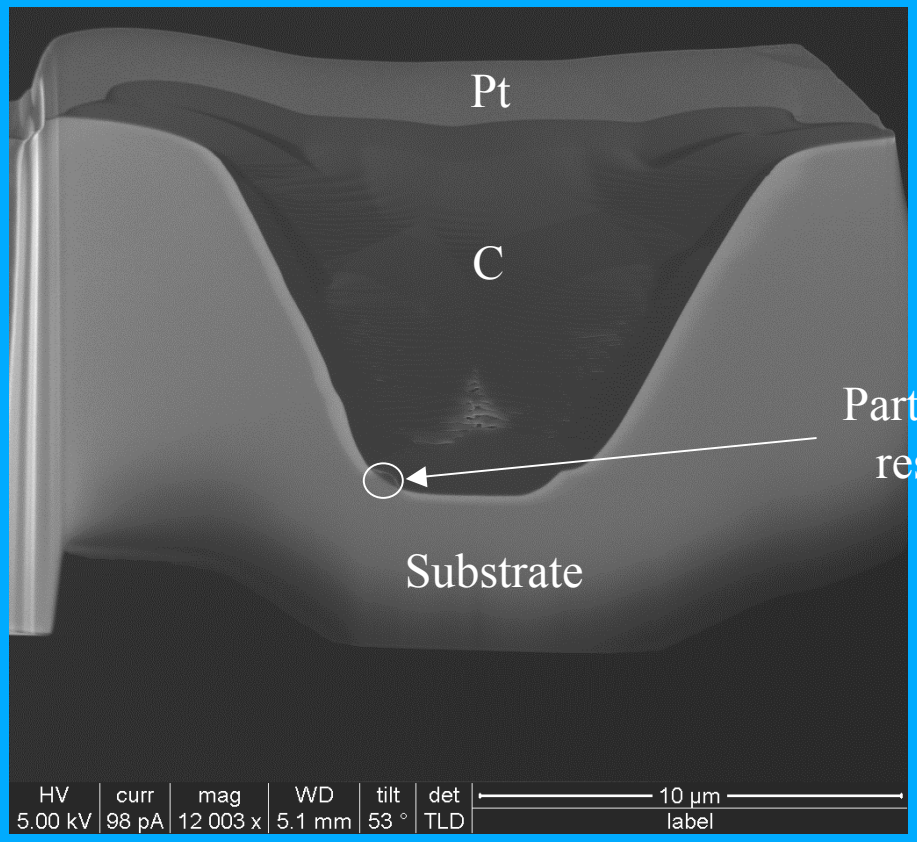
ii. FIB-TEM Section From 3-7-8-3 Side B (Cd-rich face)

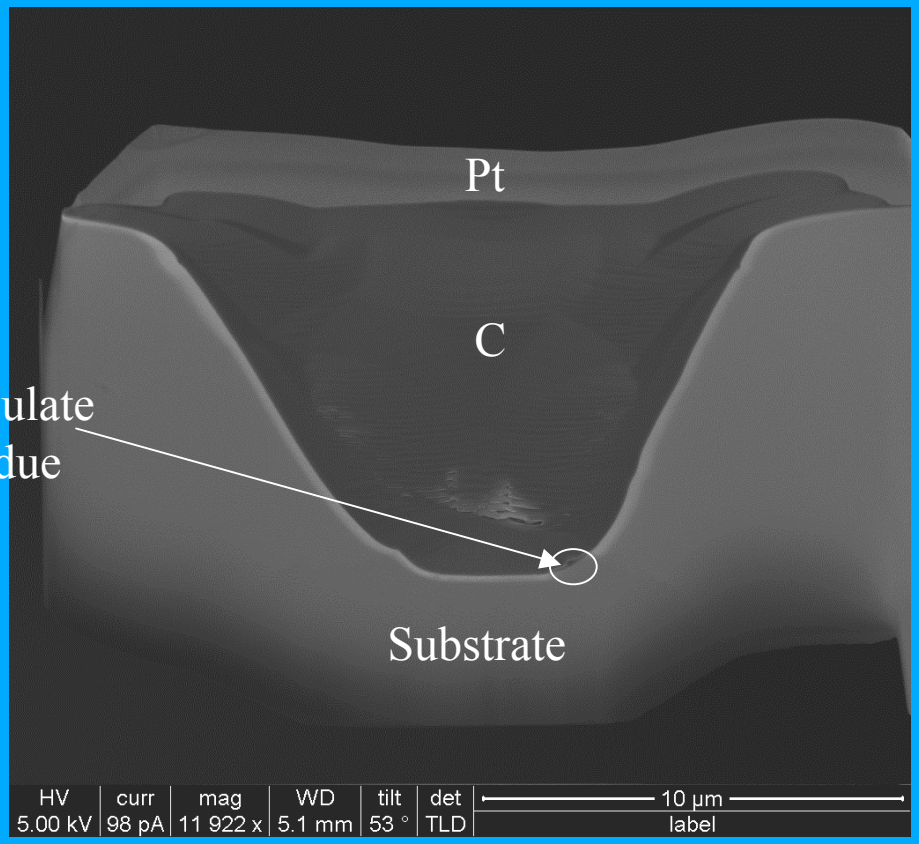
i. FIB-TEM Section From 3-7-8-3 Side A (Te-rich face) Surface Depression Feature



1.) “Pyramid” depression feature was filled in with C using the in-situ deposition capabilities of the FIB. The entire surface of the feature was then covered with Pt. Both the C and Pt layers reduce the effects of potential beam damage during the FIB milling process to produce a TEM section. 2.) The feature after the ion beam has trenched either side of the Pt strap – this reveals a cross-sectional view of the sample. 3) The section is further thinned to approximately 1 micron thick and then the ion beam is used to make sidewall and under-cuts to enable the extraction of the section. 4) The in-situ extraction of the section from the bulk material. 5.) The section after it has been attached to the TEM grid. 6) The section after further ion thinning has resulted in a section approximately 100 nm thick.

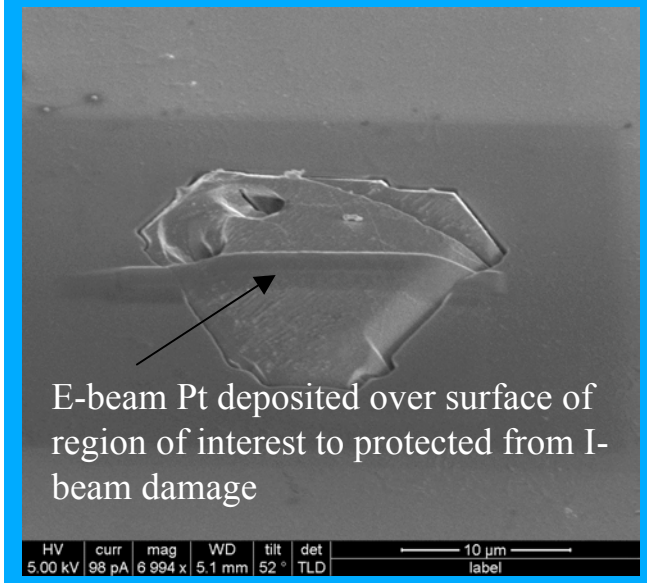
FIB-TEM Section (3-7-8-3 Side A)

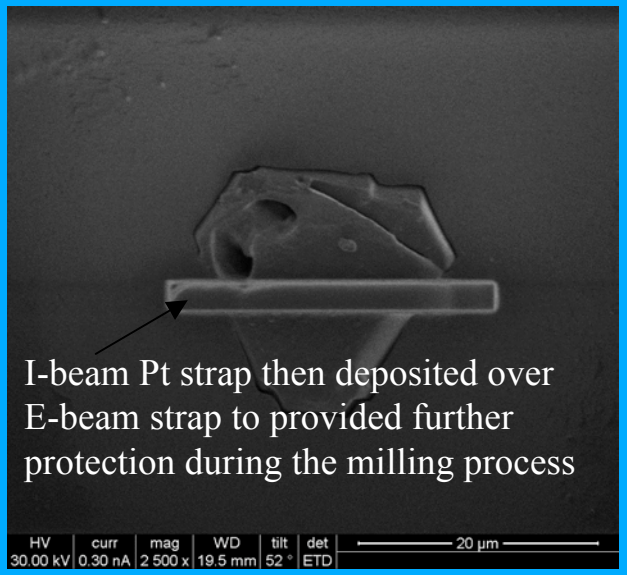


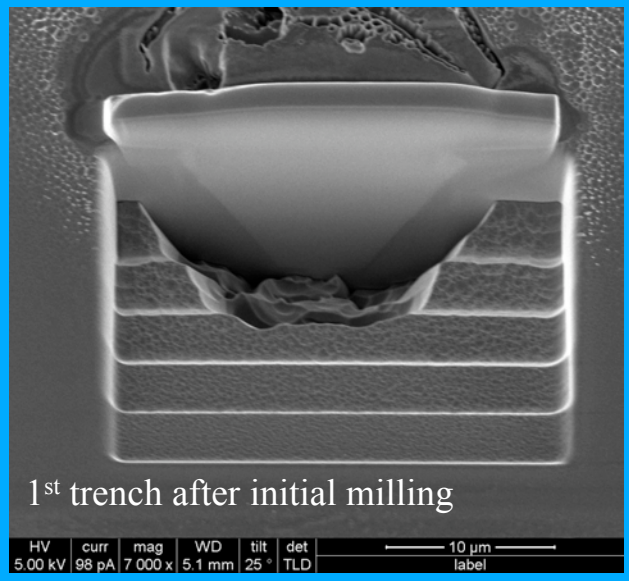


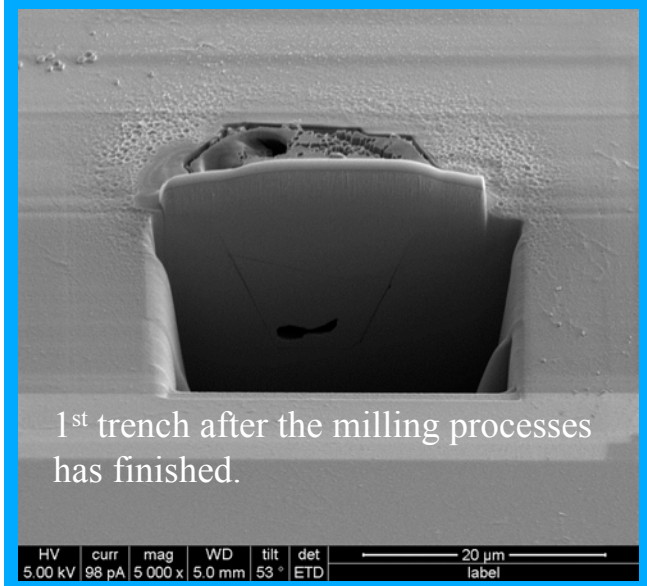
5 kV secondary electron imaging of the front and backside of the electron transparent section.

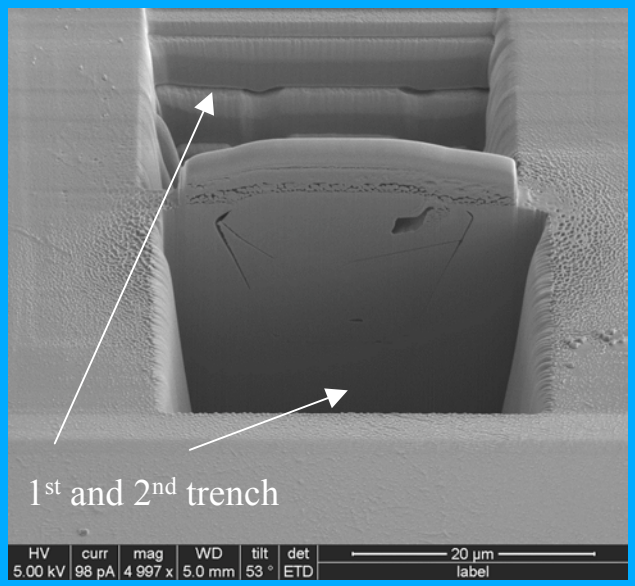
i. FIB-TEM Section From 3-7-8-3 Side A (Te-rich face) Raised Surface Feature

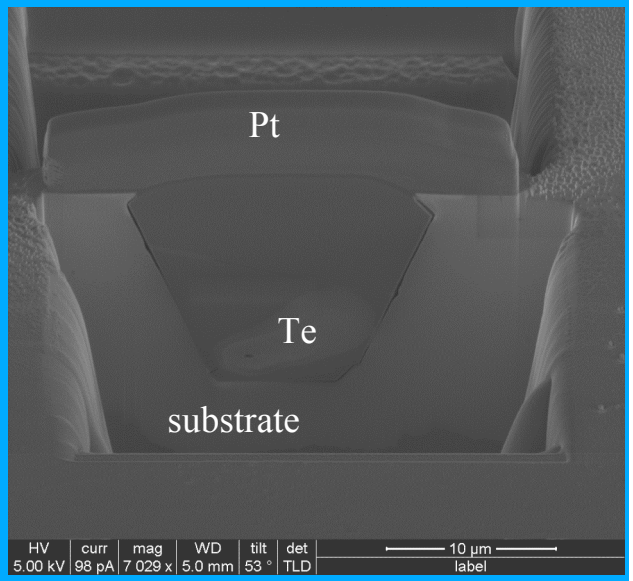




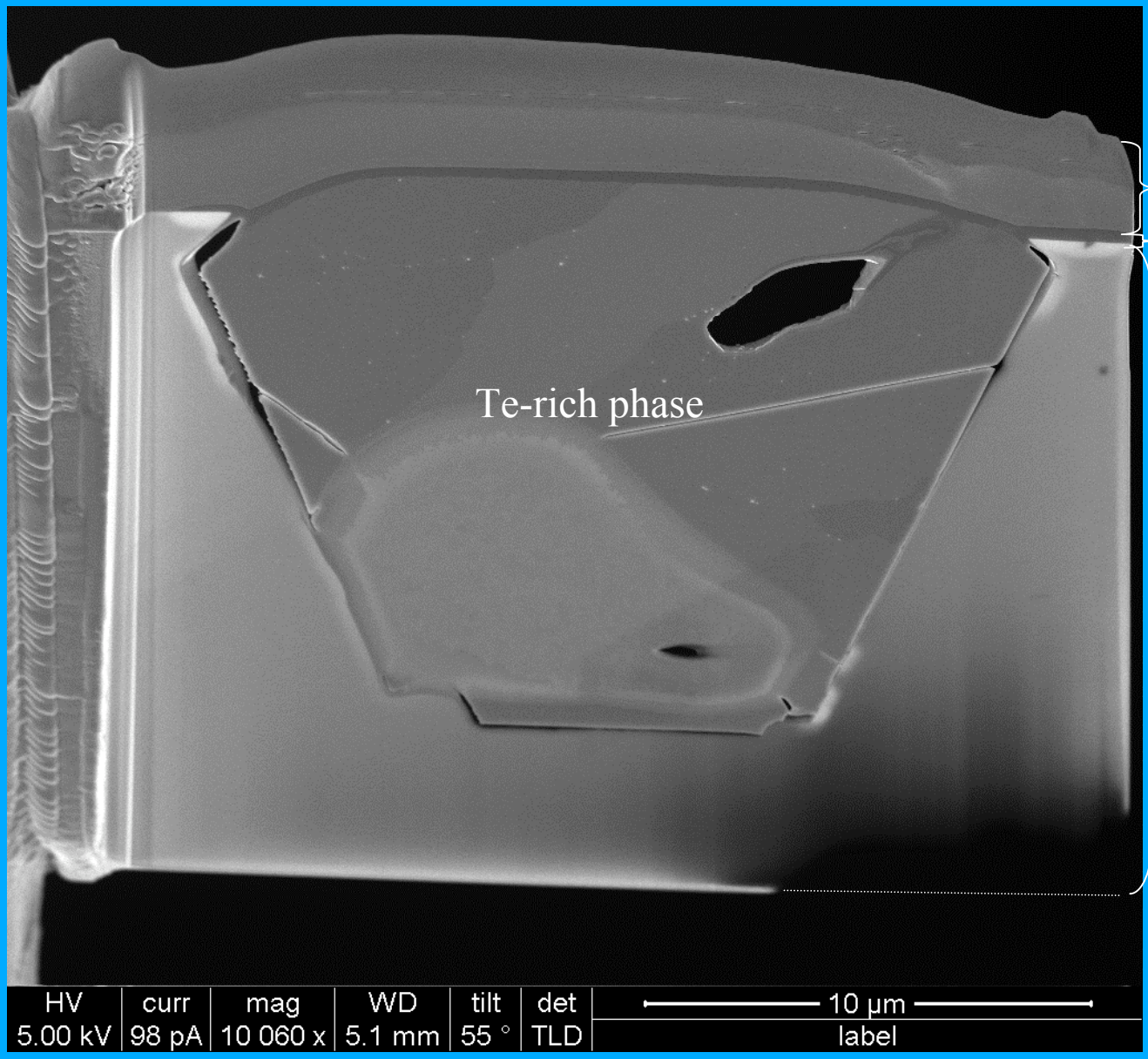






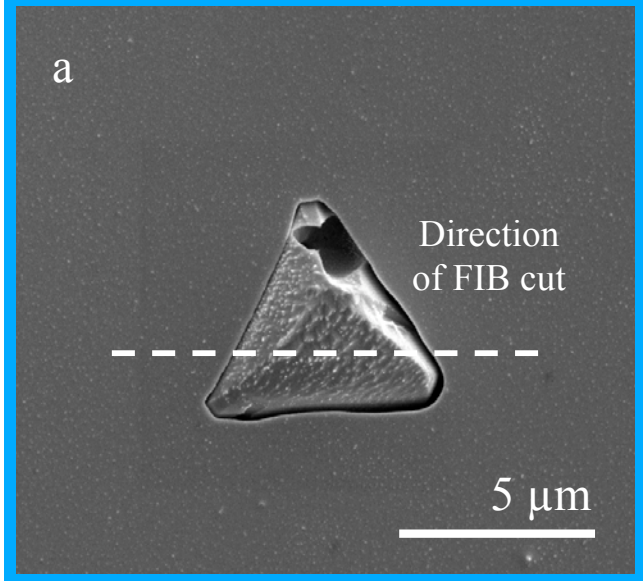


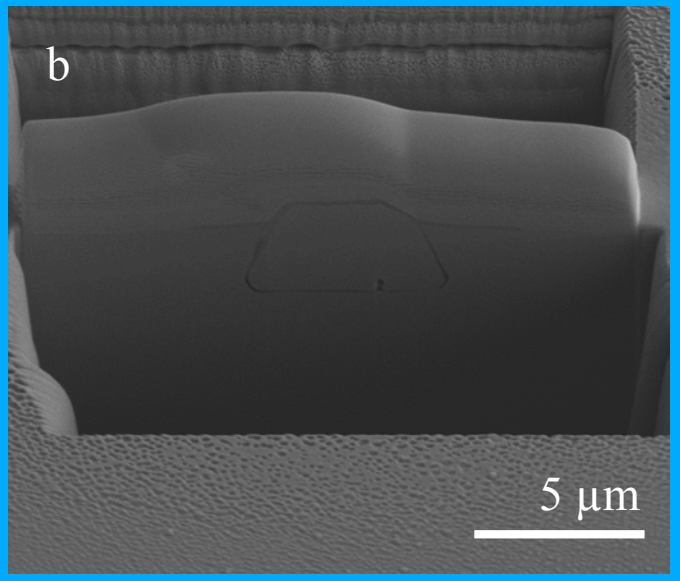
FIB-TEM Section (Sample CZT3-7-8-3 Side A)

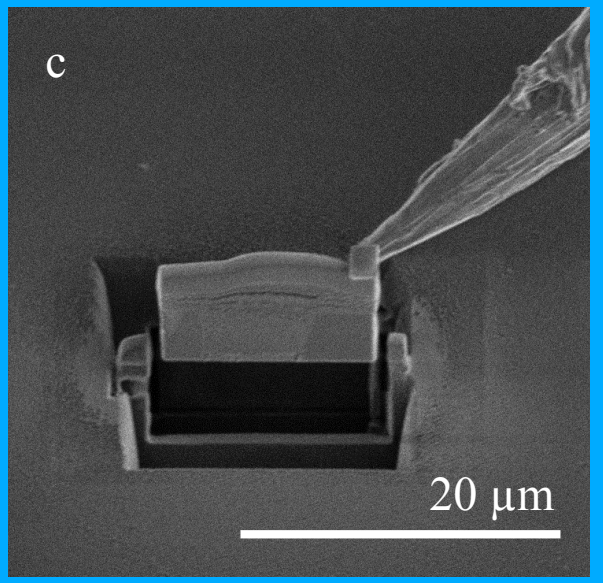


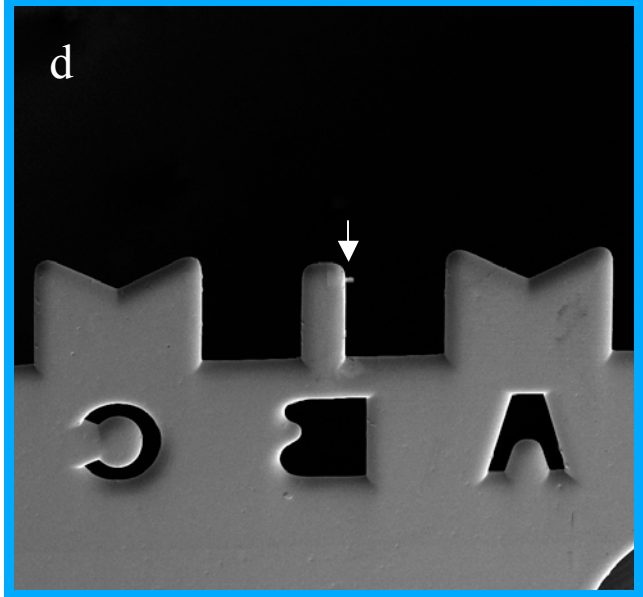
5 kV secondary electron image acquired using an FEI Nova 600 Dualbeam FIB-FESEM

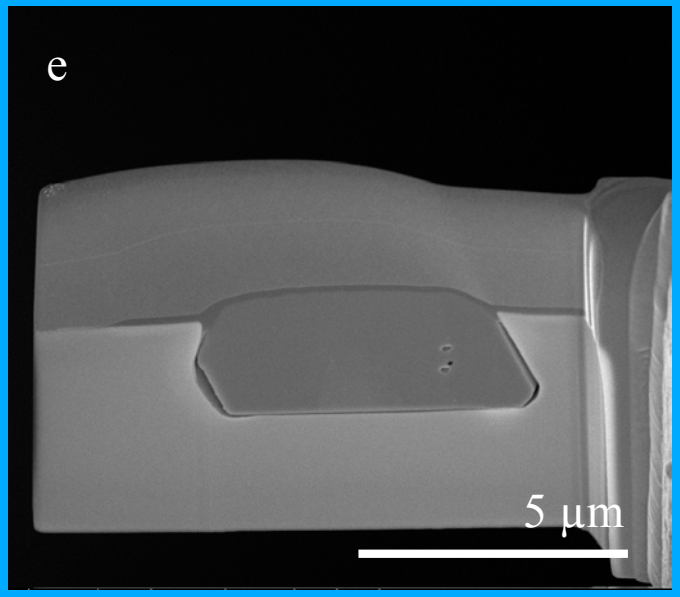
ii. FIB-TEM Section From 3-7-8-3 Side B (Cd-rich face)







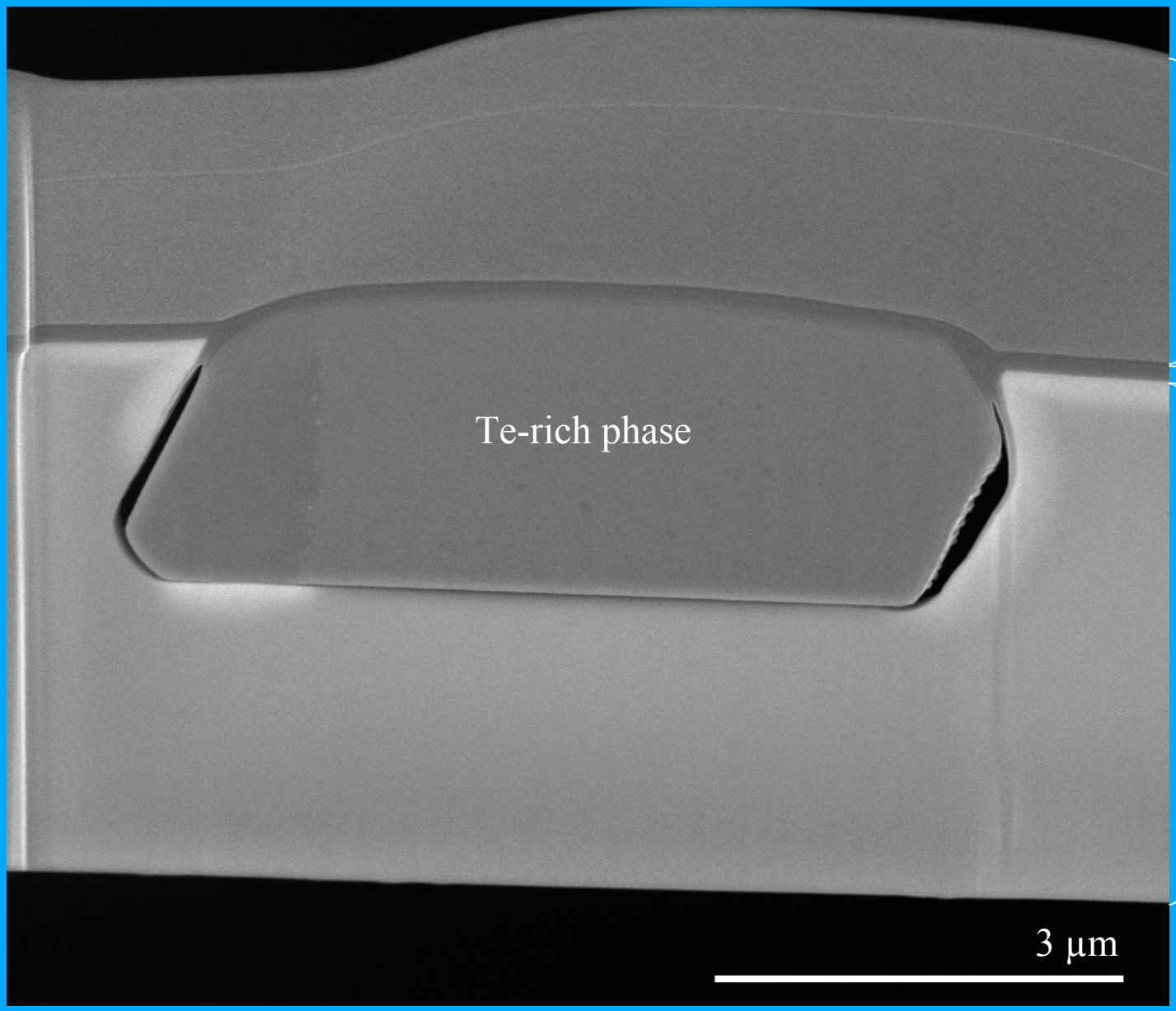




a) Feature prior to FIB milling.
b) Feature 2 after initial milling. Region of interest is protected with a Pt layer.
c) Feature 2 during in situ liftout.
d) FIB section mounted onto the grid.
e) Section after further FIB milling has reduce the thickness to electron transparency.

(Images a, b, c, d & e acquired at 5 kV and in secondary electron mode. Image c is a 30 kV ion induced secondary electron image – both acquired using an FEI Nova 600 Dualbeam FIB-FESEM)

FIB-TEM Section of Feature 2 (Sample CZT3-7-8-3 Side B)



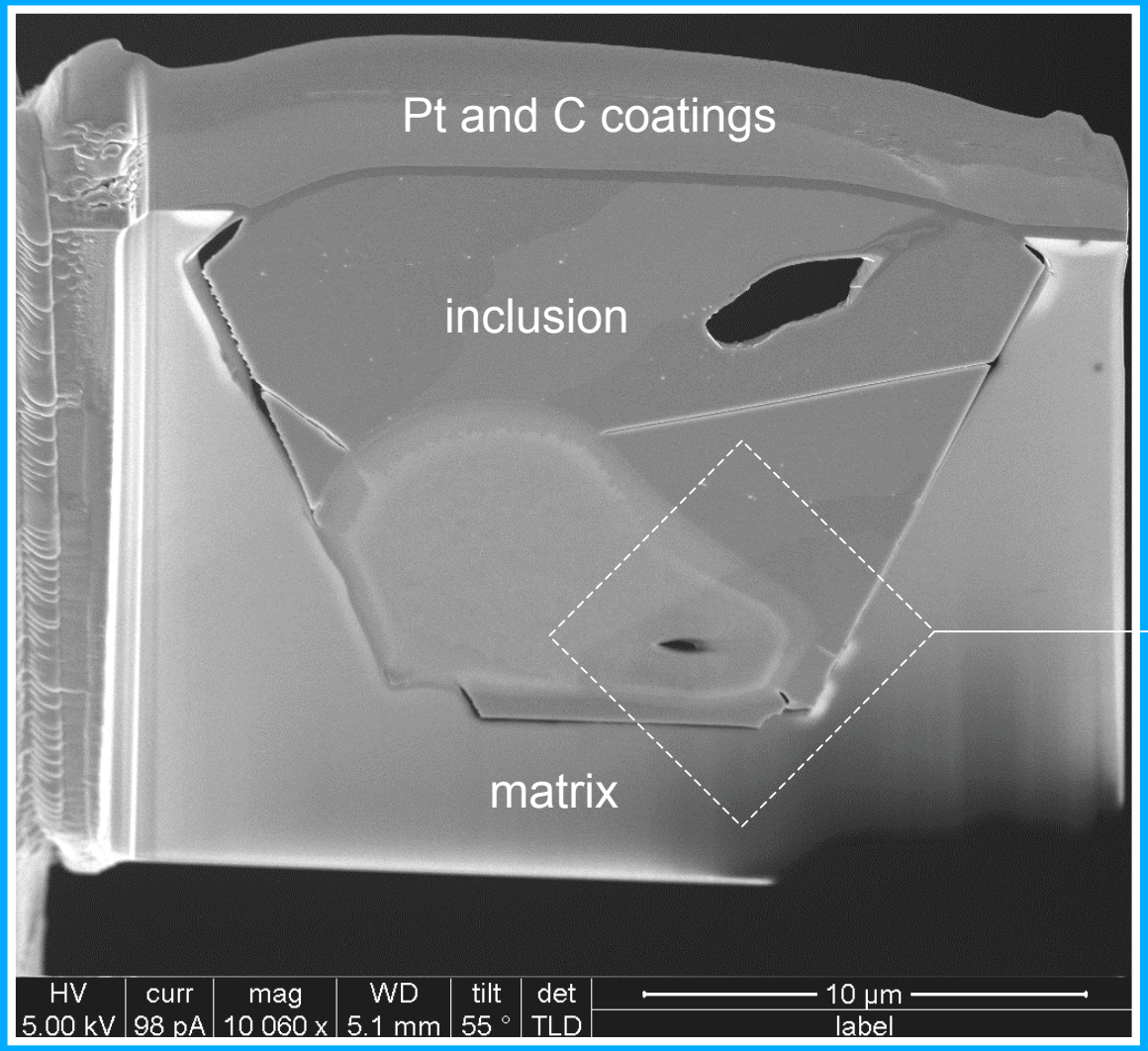
5 kV secondary electron image acquired using an FEI Nova 600 Dualbeam FIB-FESEM

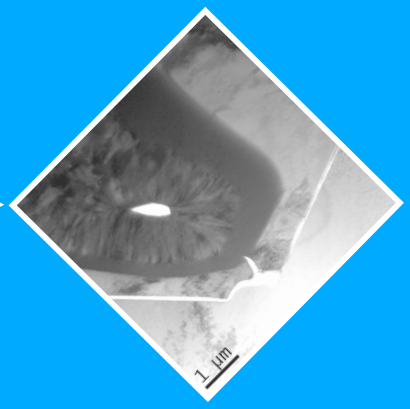
3. TEM Studies

i. FIB-TEM Section From 3-7-8-3 Side A (Te-rich face)

ii. FIB-TEM Section From 3-7-8-3 Side B (Cd-rich face)

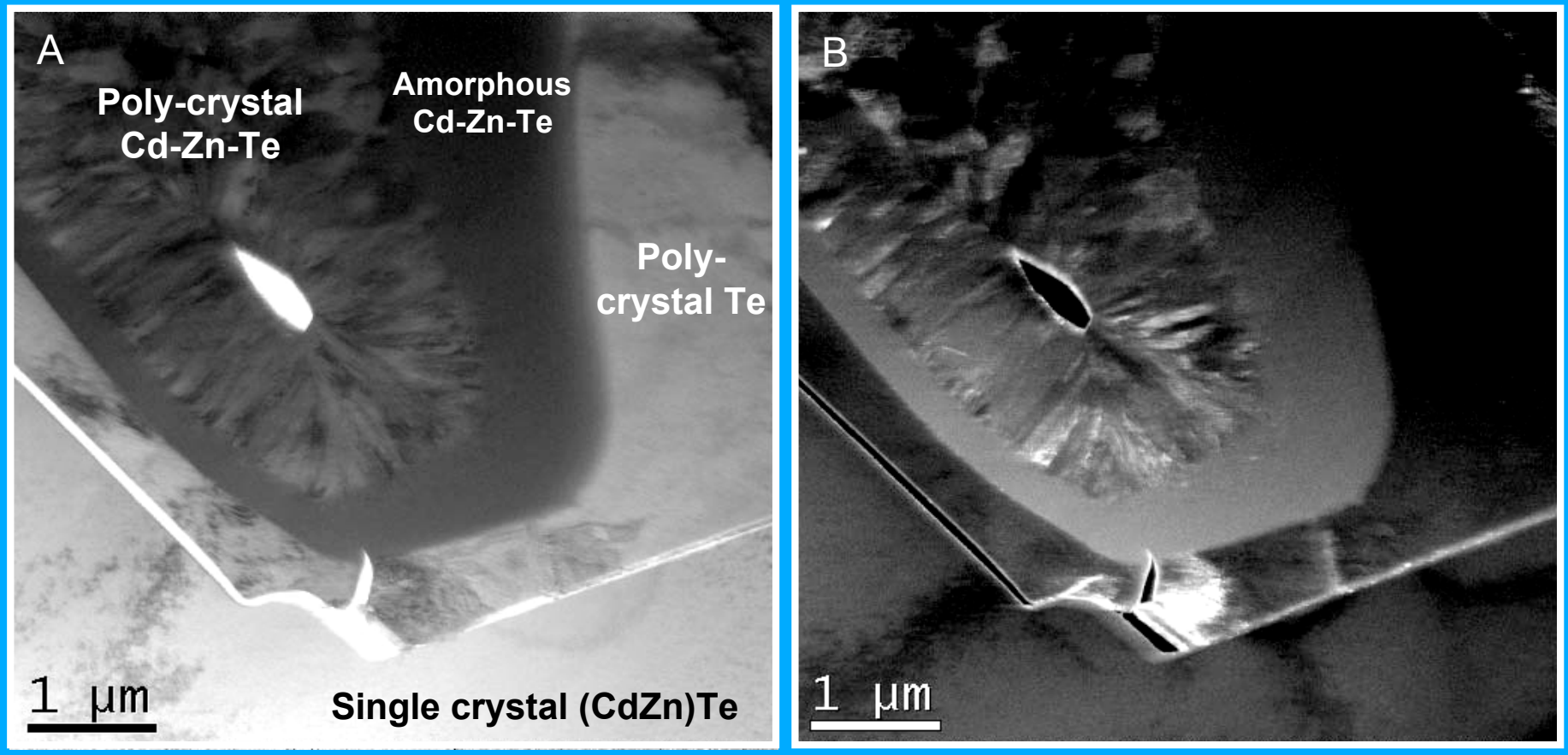
i. FIB-TEM Section From 3-7-8-3 Side A (Te-rich face)



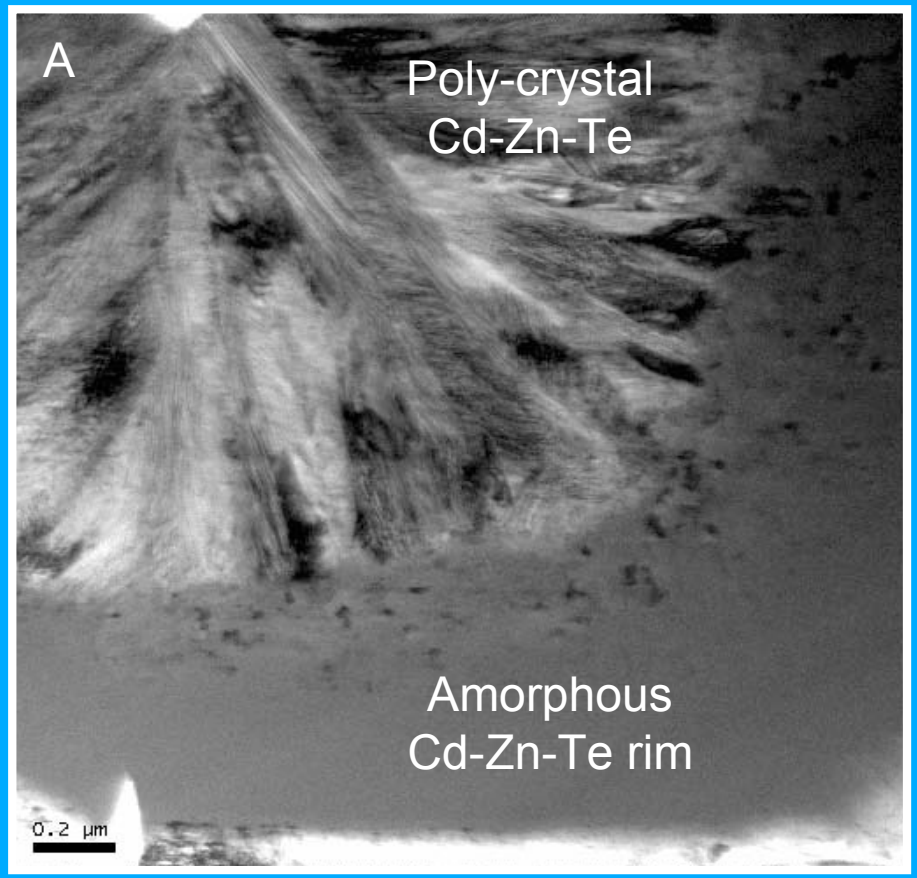


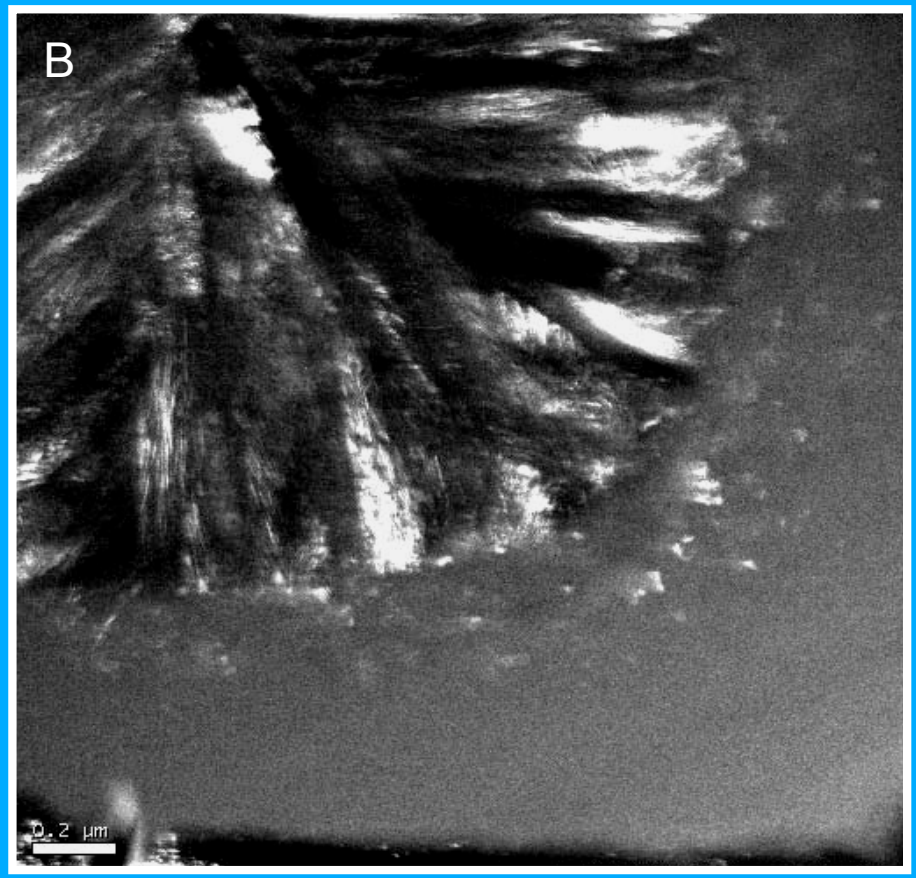
TEM BF image

Secondary electron SEM image of TEM sample prepared by FIB, in which an "inclusion" inserts into the matrix phase. TEM analysis has been made to the area enclosed in the dashed line box marked on the image.

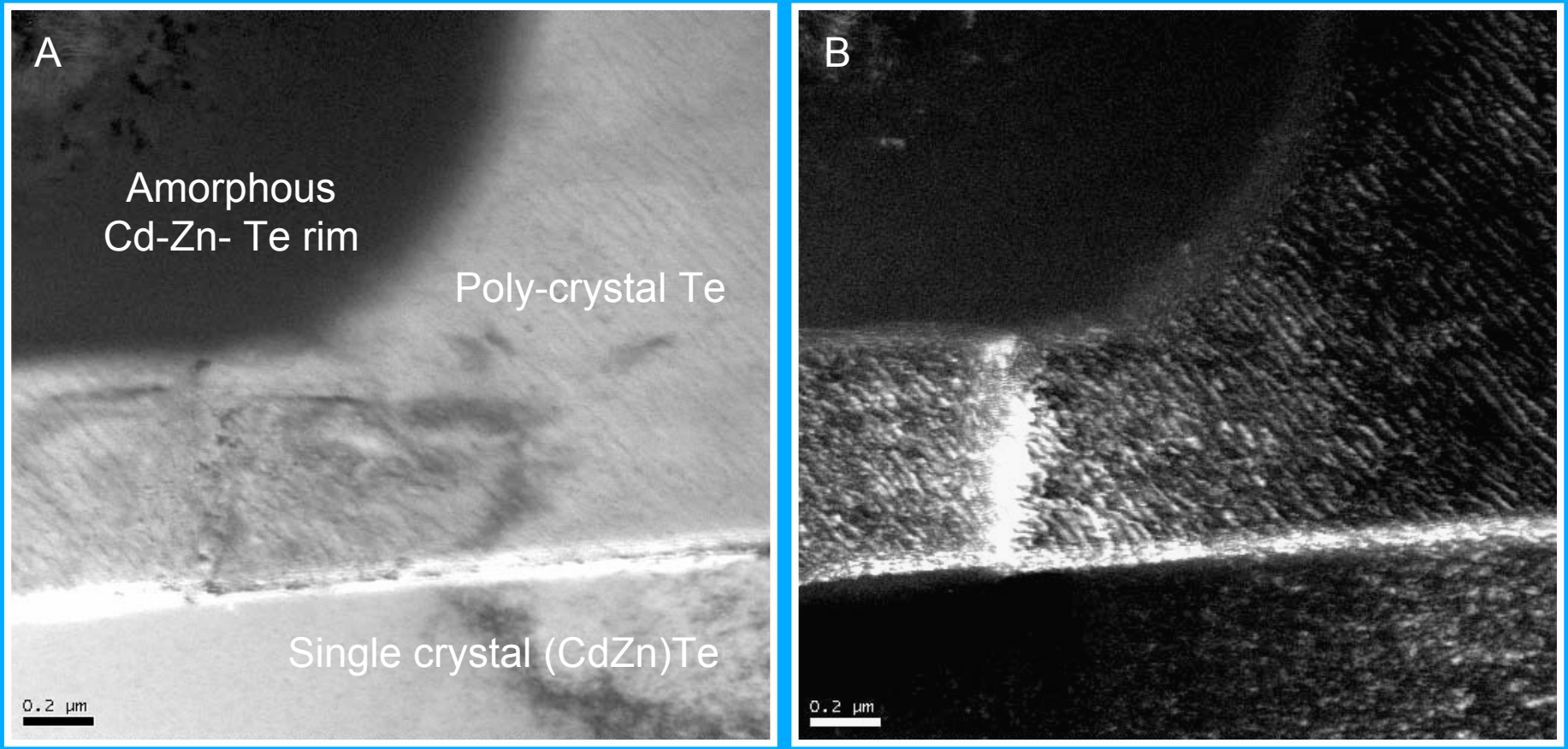


Bright-field (BF) (A) and dark-field (DF) (B) TEM images that show the single crystal matrix phase (CdZn)Te and a part of the "inclusion". The "inclusion" consists of a crystalline matrix (Te) and a "sub-inclusion" composing polycrystalline phase(s) and an amorphous rim. The "inclusion" mechanically separates from the single crystal (CdZn)Te matrix.

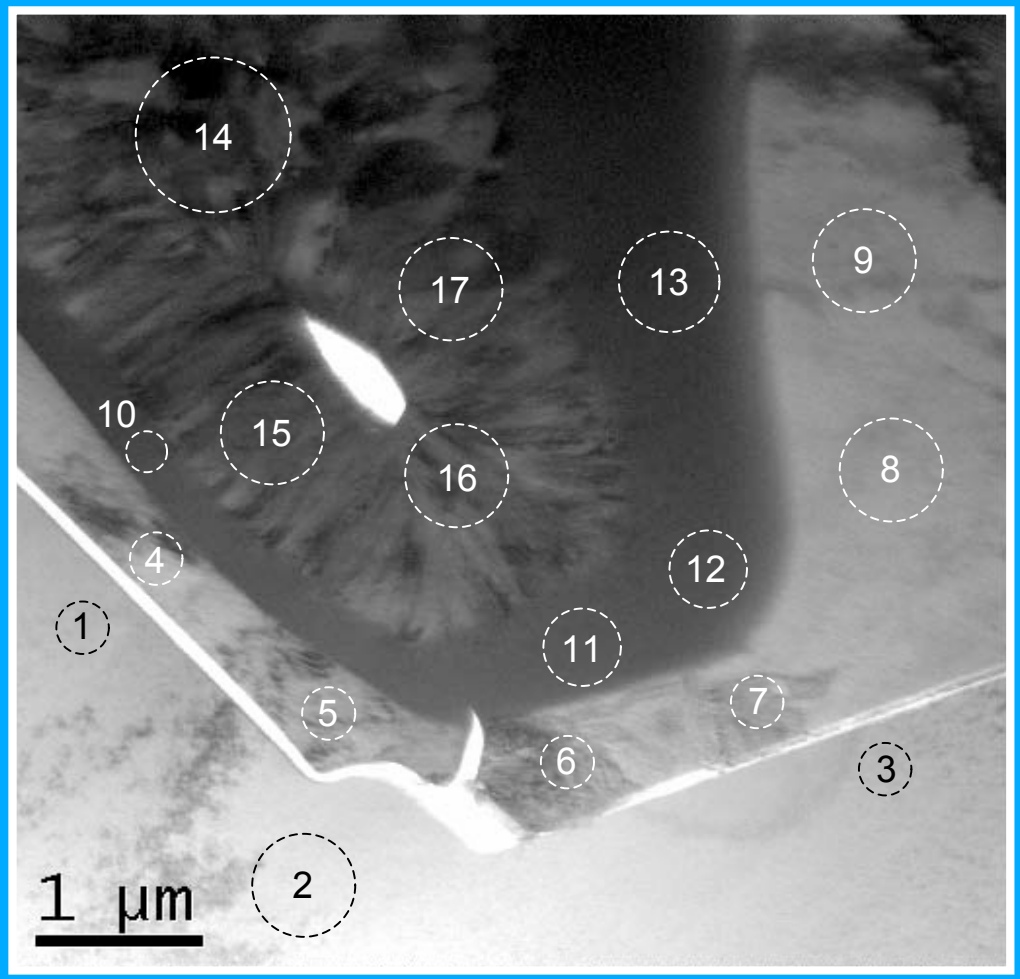




Enlarged BF (A) and DF (B) TEM images that show the interface between the polycrystalline stuff and the amorphous rim. EDS analysis (see the following) indicates that the amorphous rim contains lower abundance of Cd than that in the polycrystalline stuff. Average atomic percentage of Cd+Zn is less than that of Te in the polycrystalline stuff, indicating it may not consist of one single phase.



Enlarged BF (A) and DF (B) TEM images that show the interfaces of amorphous rim/crystalline Te and crystalline Te/single crystal (CdZn)Te. The crystalline Te mechanically separates from the single crystal (CdZn)Te matrix.

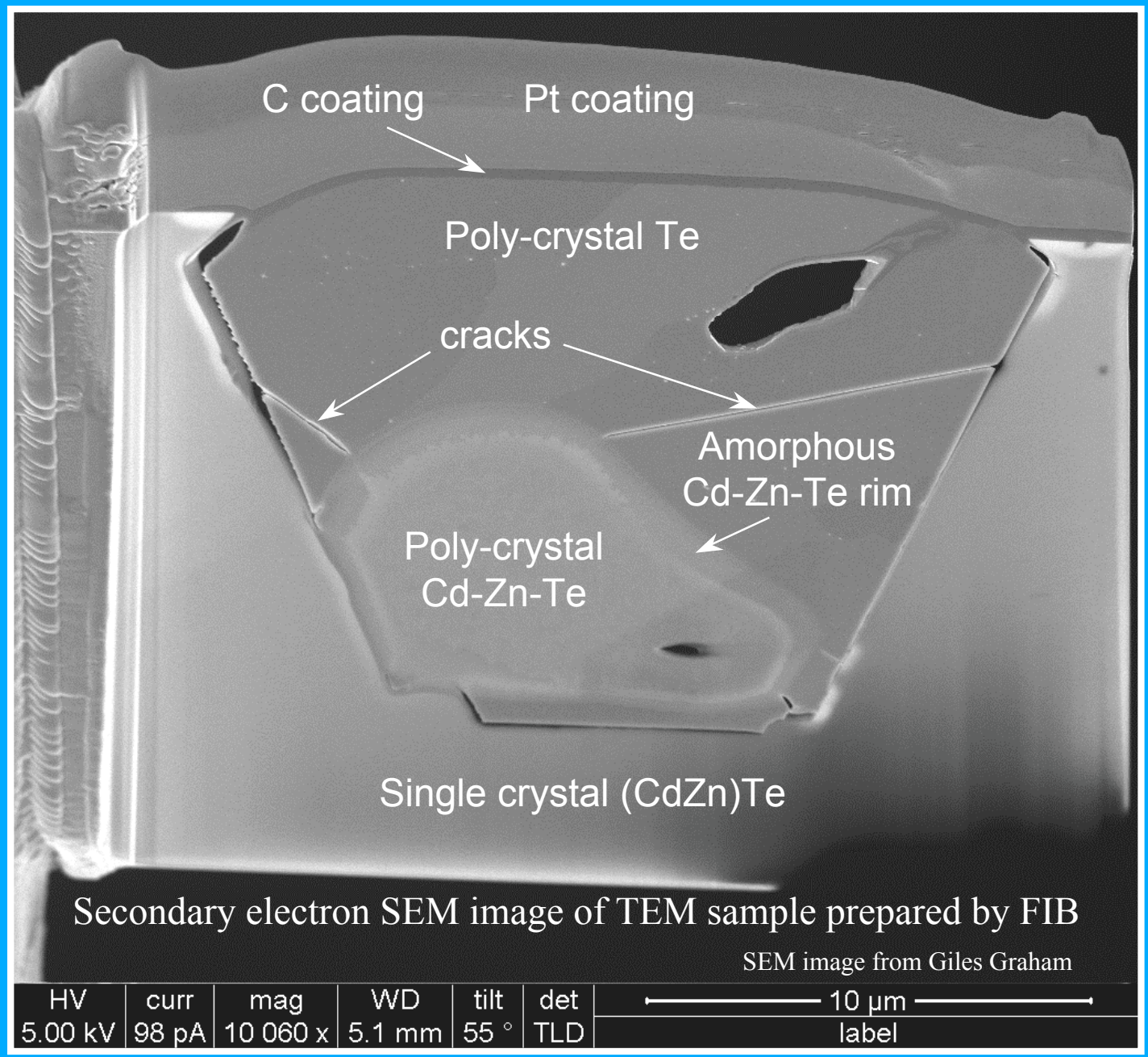


X-ray EDS analysis

- Single crystal matrix: $(Cd_{1-x}Zn_x)Te$ (x~0.13)
- Ploycrystal Te having a surface oxidation.
- Amorphous rim: $(Cd_{0.48}Zn_{0.08})Te$ ((Cd+Zn)/Te ~ 0.5)
- Polycrystalline phases: $(Cd_{0.78}Zn_{0.10})Te$ ((Cd+Zn)/Te ~ 0.88)

Composition analysis by X-ray EDS

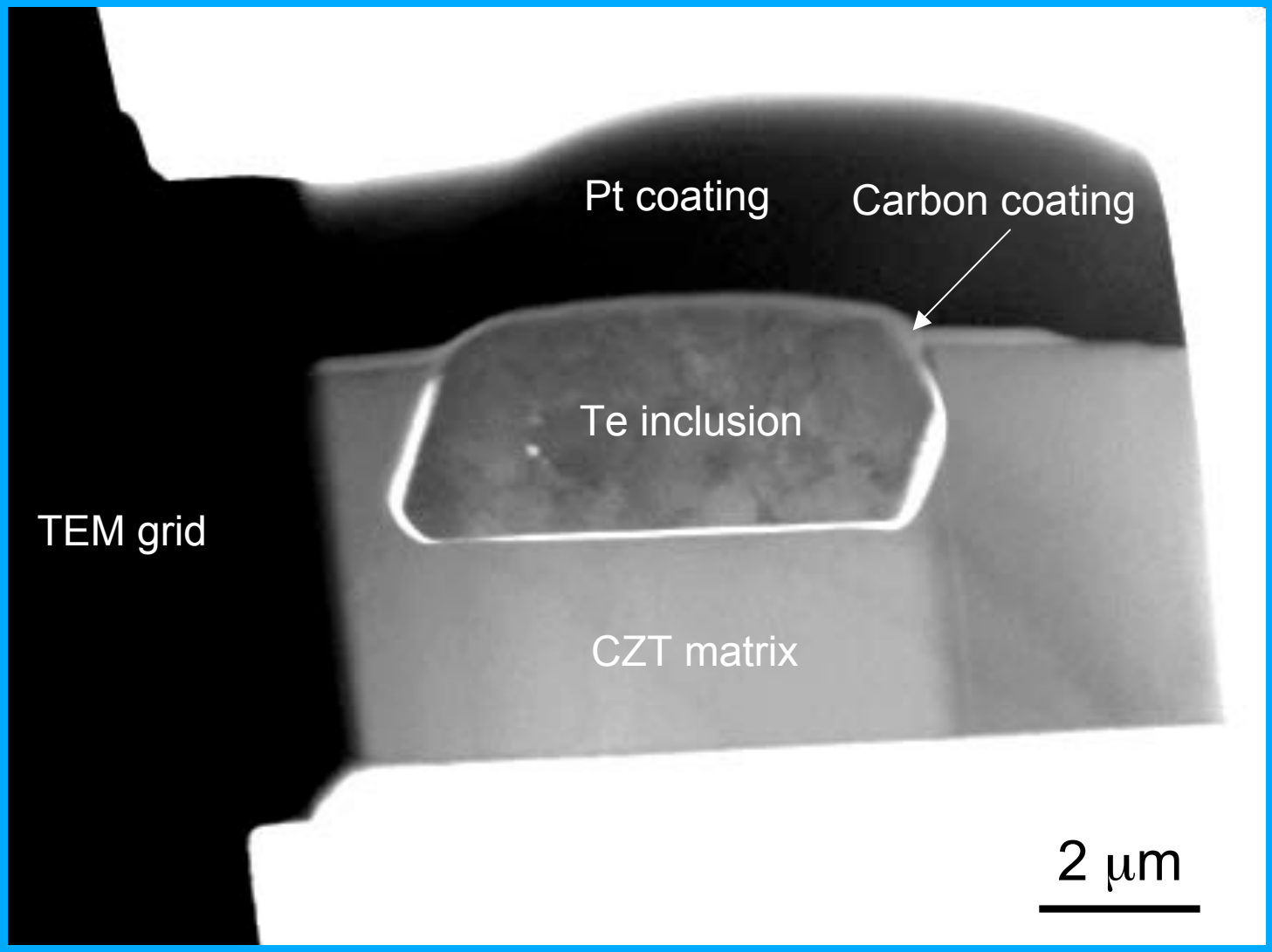
Area #	Cd (At%)	Zn (At%)	Te (At%)	O (At%)	Ref.
1	42.58	7.00	48.81	1.60	EDX-5
2	42.52	6.34	49.07	2.06	EDX-1
3	42.16	6.04	49.85	1.94	EDX-8
average	**42.42**	**6.46**	**49.24**	**1.87**	**(CdZn)Te**
4	0.00	0.00	92.15	7.85	EDX-4
5	0.00	0.00	90.51	9.49	EDX-2
6	0.00	0.00	92.00	8.00	EDX-3
7	0.00	0.00	90.90	9.10	EDX-6
8	0.00	0.00	93.05	6.95	EDX-7
9	0.00	0.00	90.74	9.26	EDX-16
average	**0.00**	**0.00**	**91.56**	**8.44**	**Poly-cryt Te**
10	32.59	5.10	61.15	1.14	EDX-13
11	32.86	4.40	59.84	2.91	EDX-11
12	24.38	3.61	69.35	2.65	EDX-18
13	30.30	4.05	63.64	2.01	EDX-15
average	**30.03**	**4.29**	**63.49**	**2.18**	**Am-phase**
14	40.45	5.22	53.18	1.14	EDX-10
15	41.68	5.02	51.67	1.63	EDX-12
16	40.04	5.46	52.06	2.44	EDX-9
17	41.29	5.61	51.98	1.12	EDX-14
average	**40.86**	**5.33**	**52.22**	**1.58**	**Poly-crystal**


C coating
Pt coating
Poly-crystal Te
cracks
Amorphous
Cd-Zn-Te rim
Poly-crystal
Cd-Zn-Te
Single crystal (CdZn)Te
Secondary electron SEM image of TEM sample prepared by FIB
SEM image from Giles Graham
HV
5.00 kV
curr
98 pA
mag
10 060 x
WD
5.1 mm
tilt
55 °
det
TLD
10 µm
label

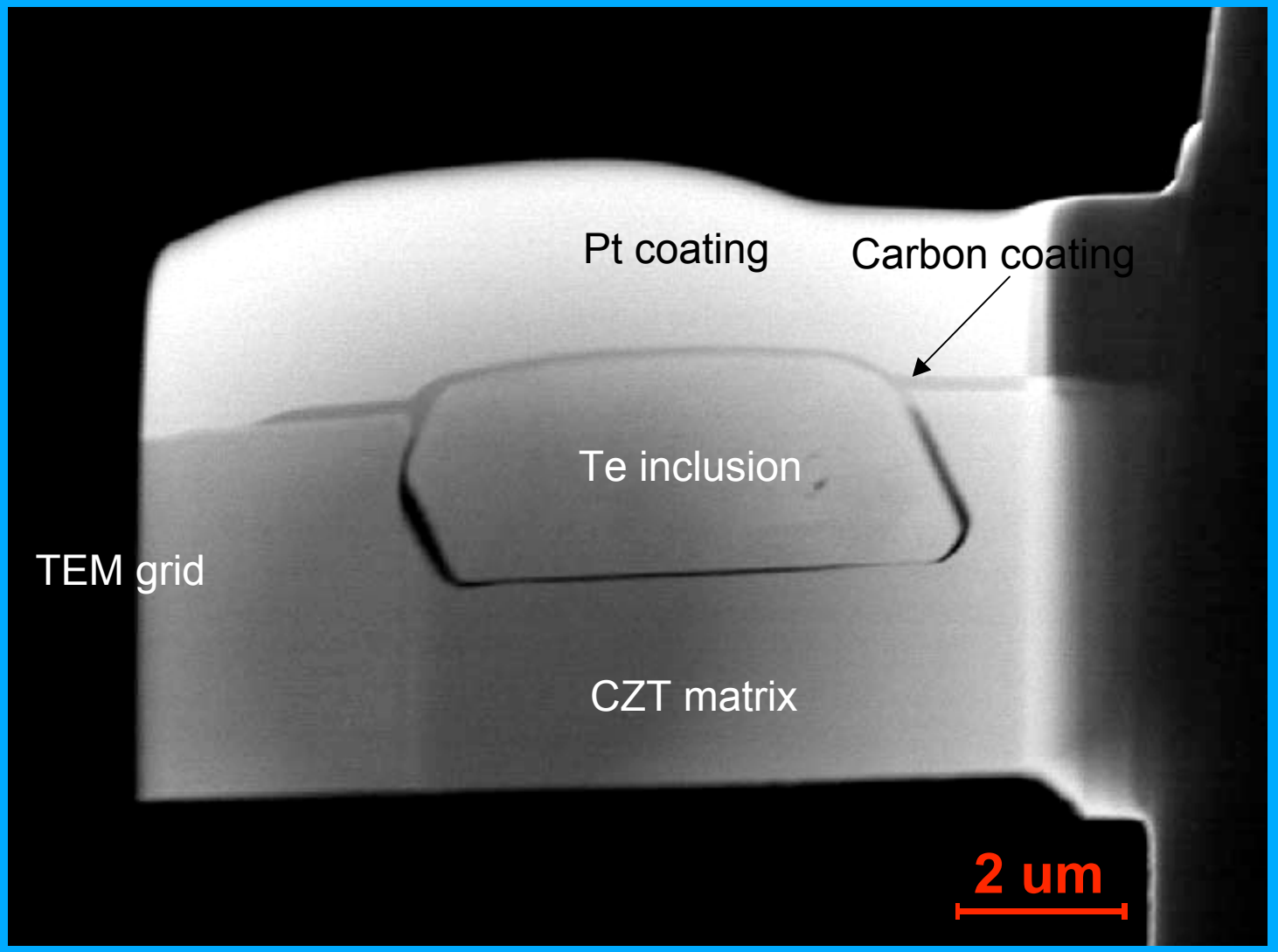
Sent to John Bradley by Zurong Dai on 07/18/2007

TEM Analysis of the Sample CZT-3-7-8-3

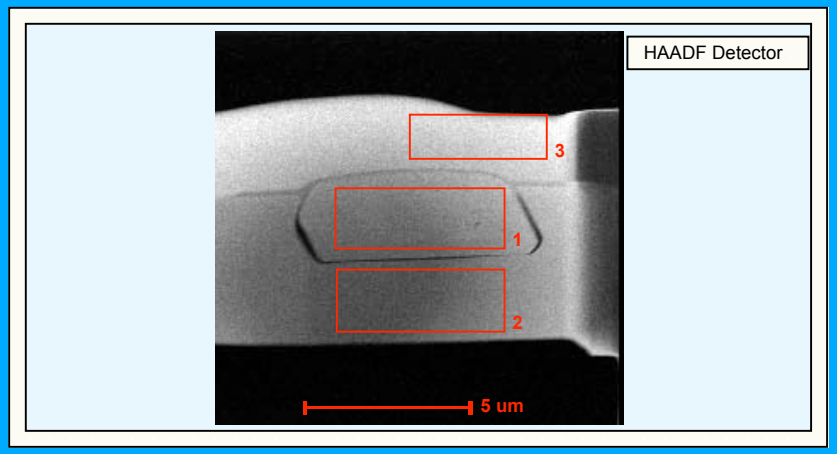
(Side B Feature 2 / FIB section)

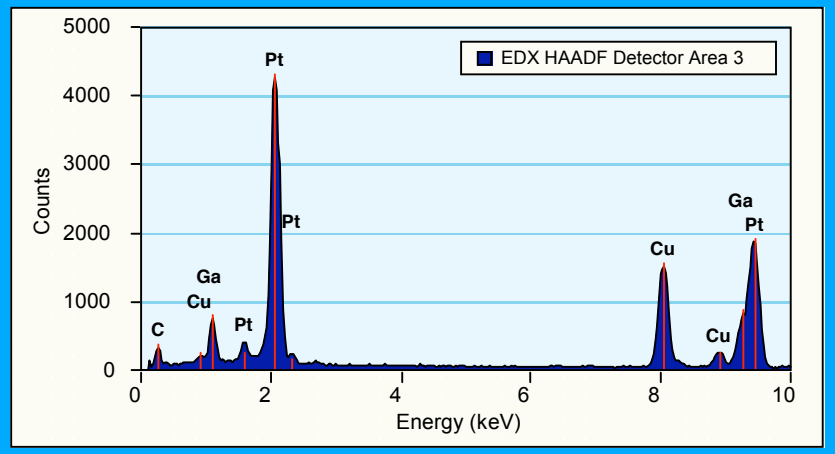


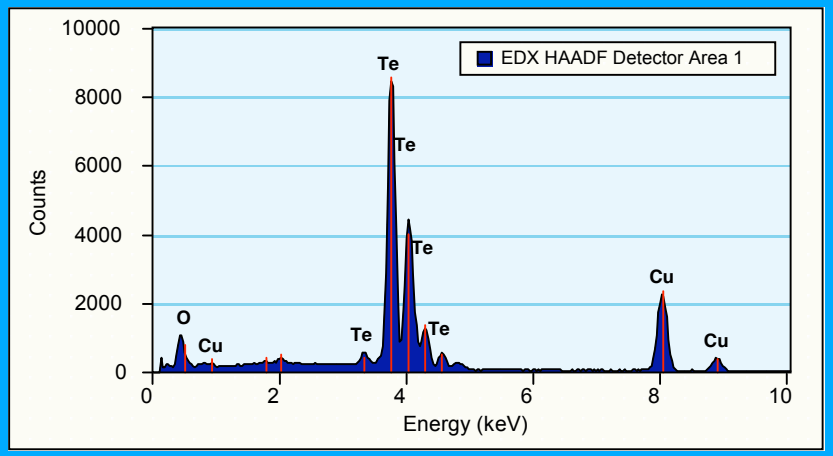
Low magnification TEM bright field image showing a morphology of FIB section

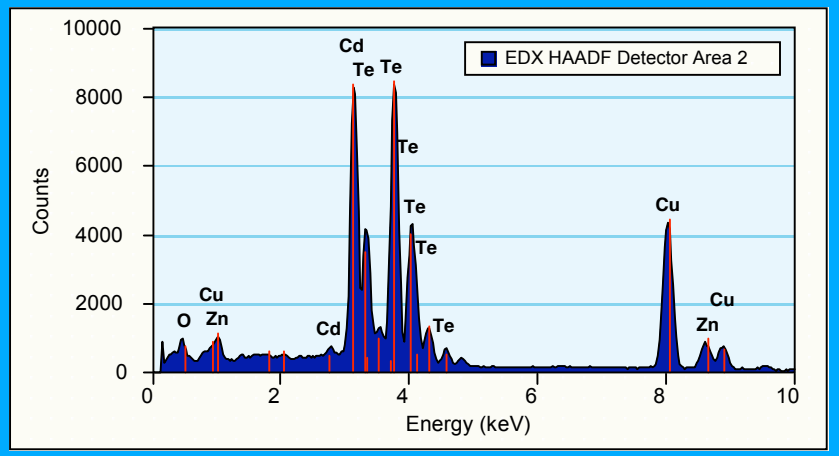


Low magnification HAADF STEM image showing a morphology of FIB section



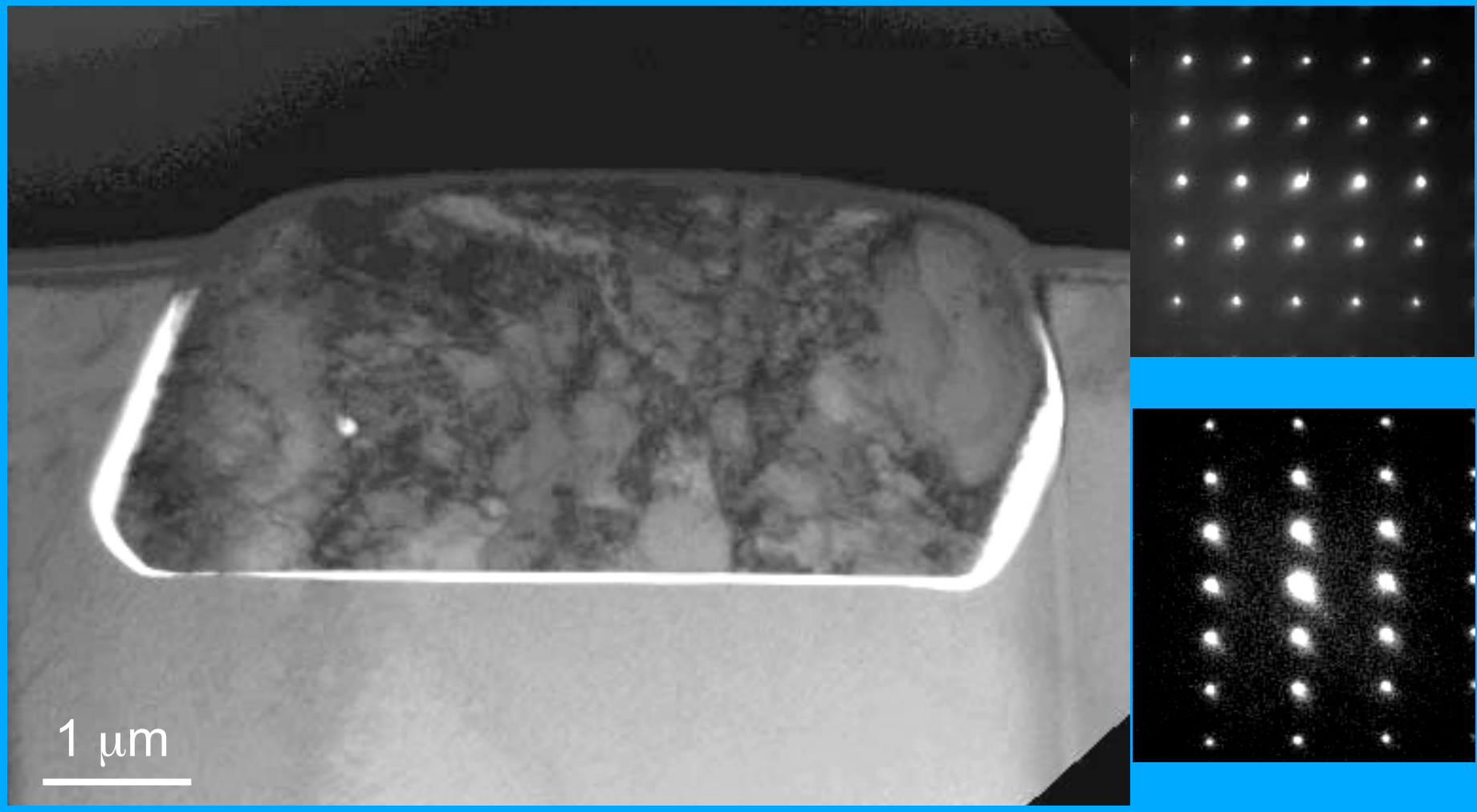






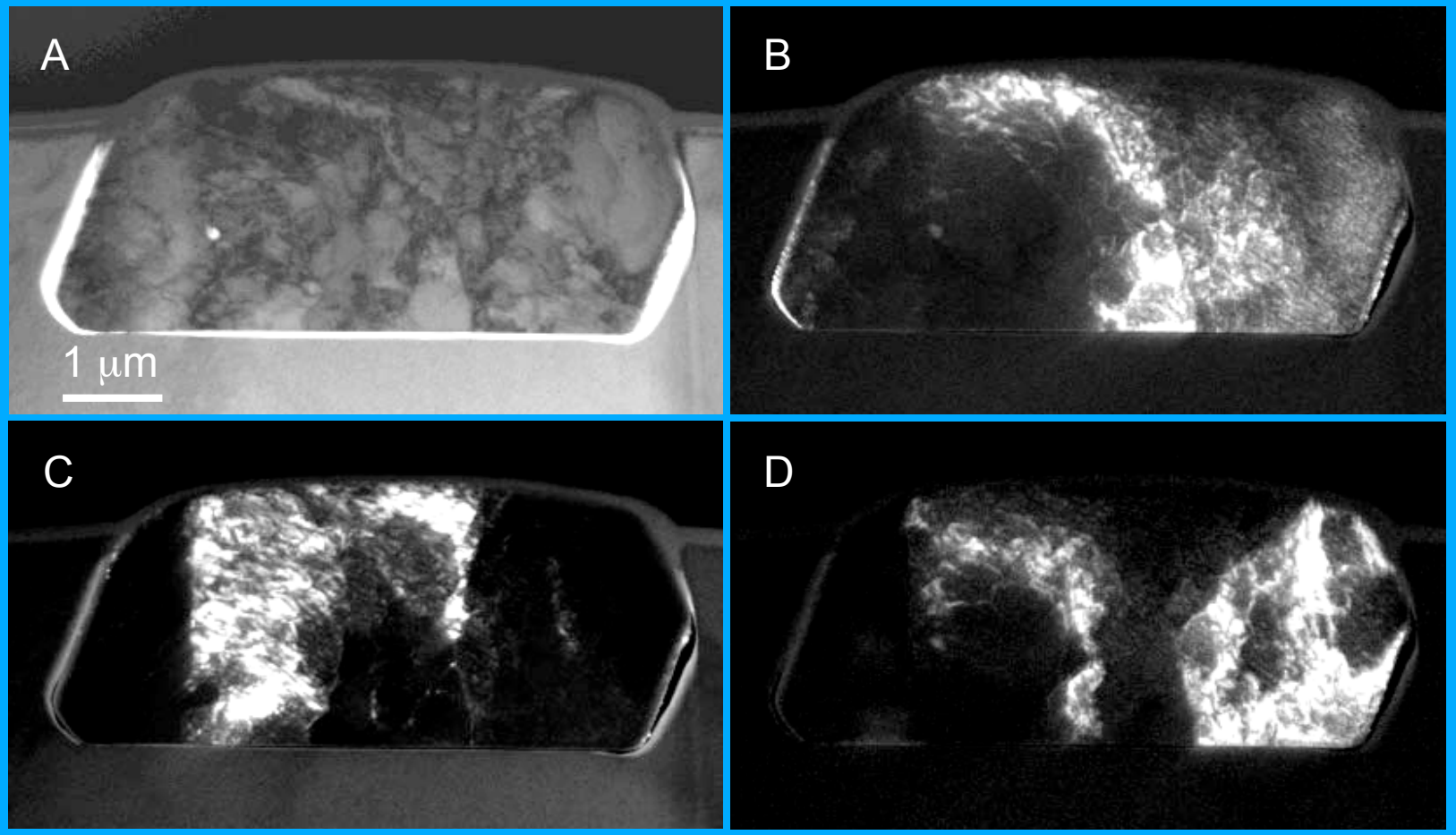
Element	Weight %	Atomic %
Zn(K)	3.917	6.988
Cd(L)	42.034	43.611
Te(L)	54.047	49.400

Composition analysis by X-ray EDS. The composition of CZT matrix is close to $(Cd_{1-x}Zn_x)Te$ with x = 0.14. Some minor elements such as Mo (or S), P?, Se?, Sn,… are also detected.



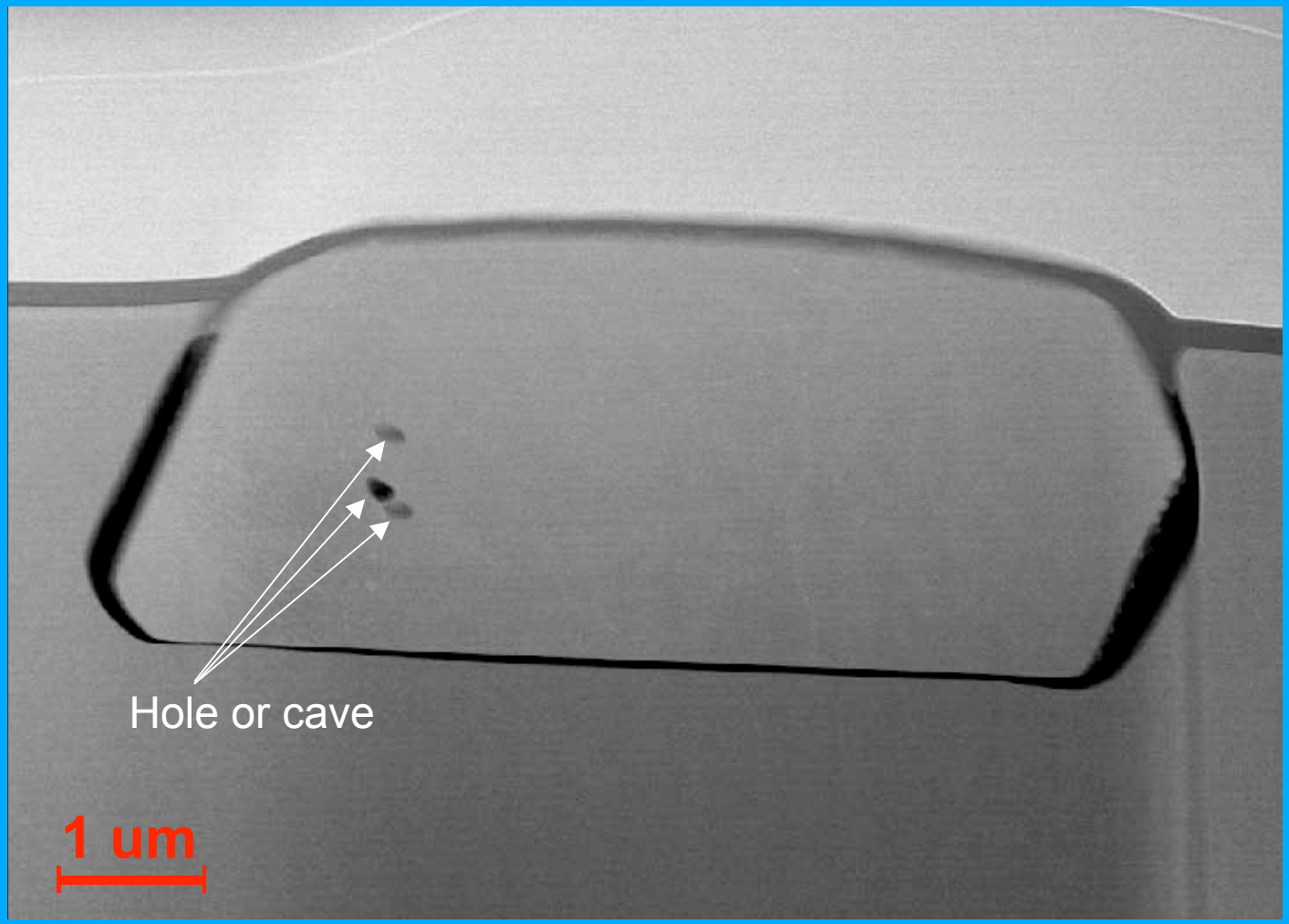
TEM bright field image showing the region around Te inclusion. The Te inclusion is characteristic of high density twine dislocations inside, a feature of plastic deformation, and separates from the single crystal CZT matrix with an abrupt surface. The crystal structure is likely rhombhedral and the Te is hexagonal but still need to be verified and index will be given soon.

Savannah River Project / Sample: CZT 3-7-8-3 (Side B Feature 2 / FIB section) / Tecnai G^2 / 07-12-2007 / LLNL

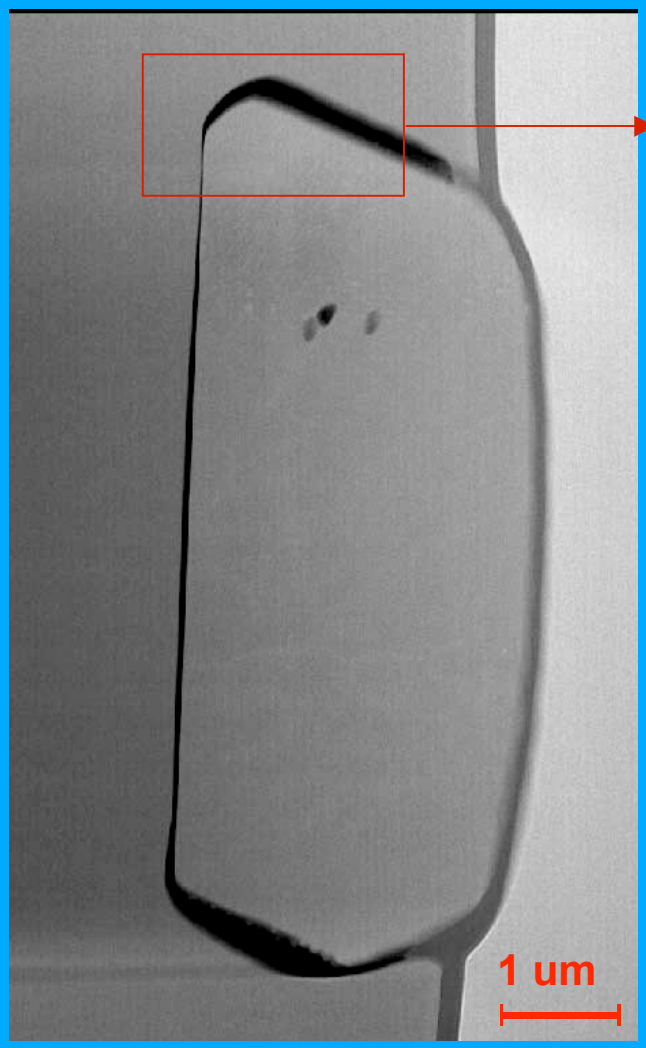


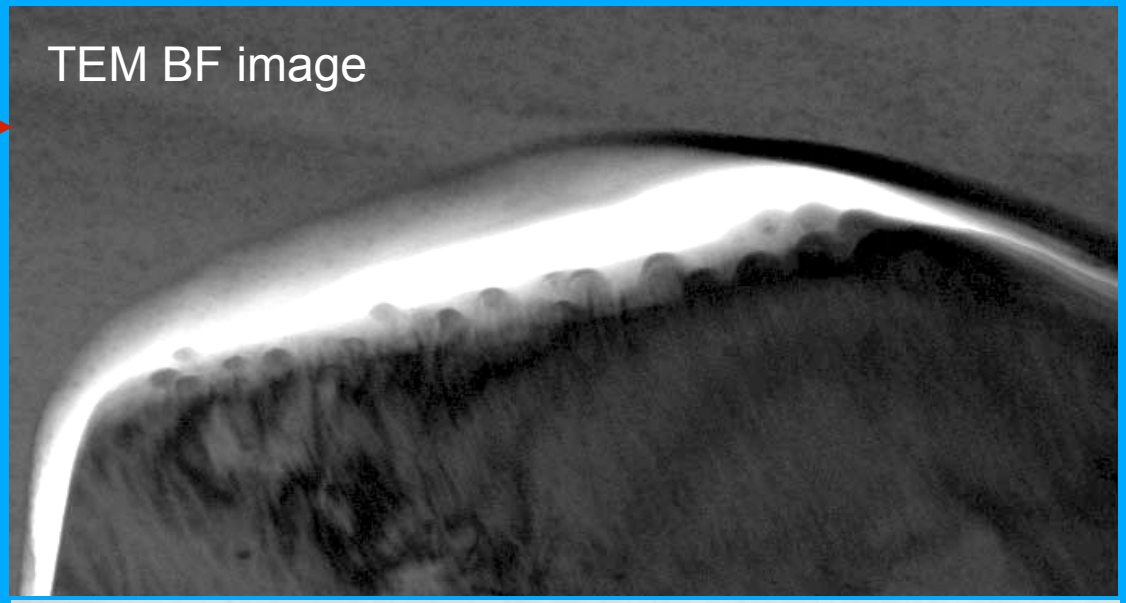
TEM bright field image (A) and dark field images (B), © and (D), which imaged by using different operation deflections. The twine dislocations, grain boundaries and sub grains can be distinguished.

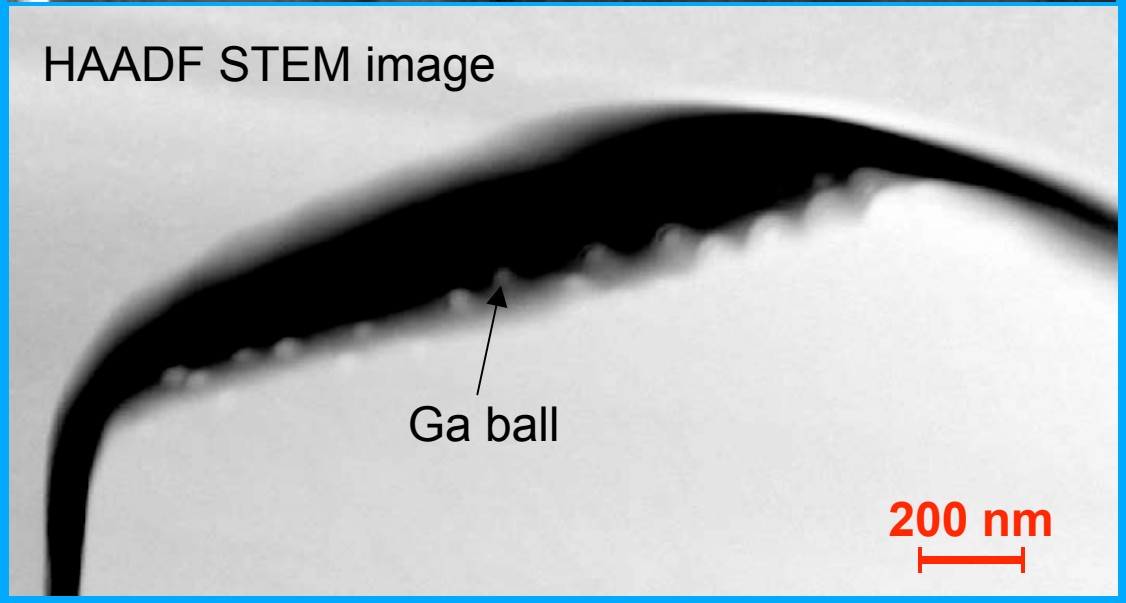
Savannah River Project / Sample: CZT 3-7-8-3 (Side B Feature 2 / FIB section) / Tecnai G^2 / 07-12-2007 / LLNL



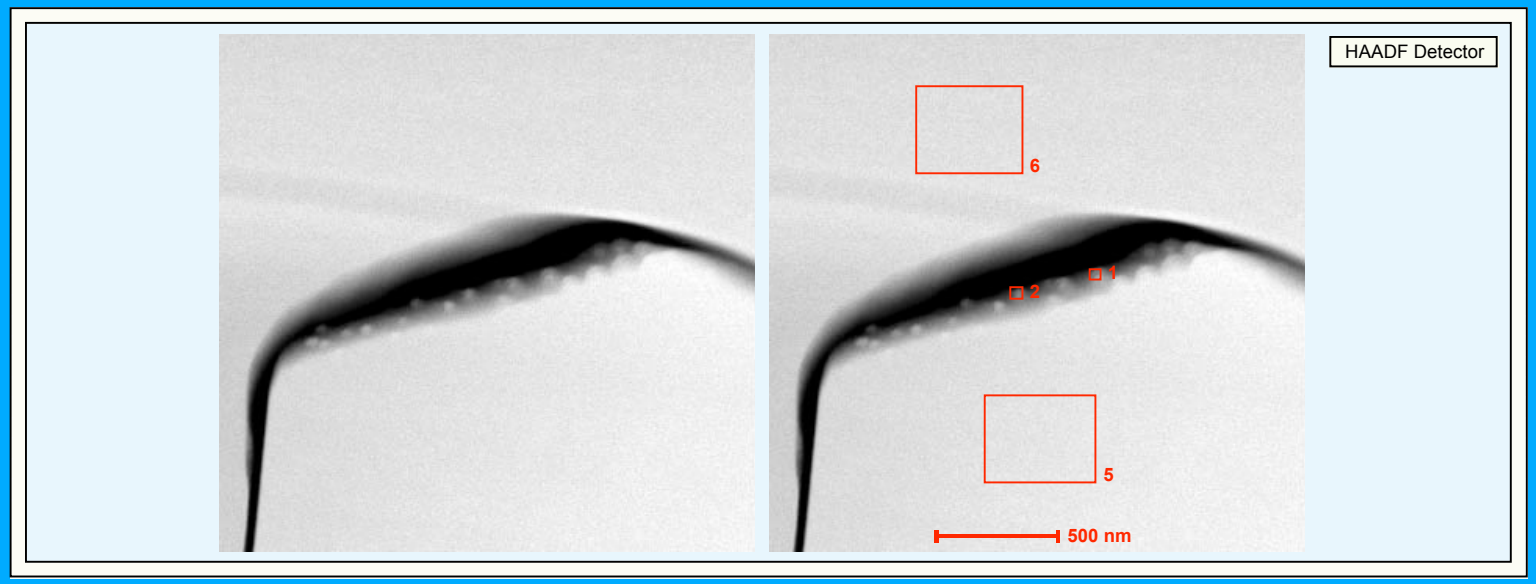
HAADF STEM image of the region around the Te inclusion.

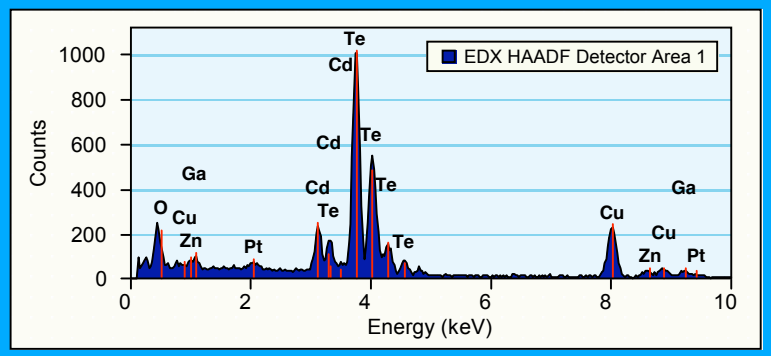


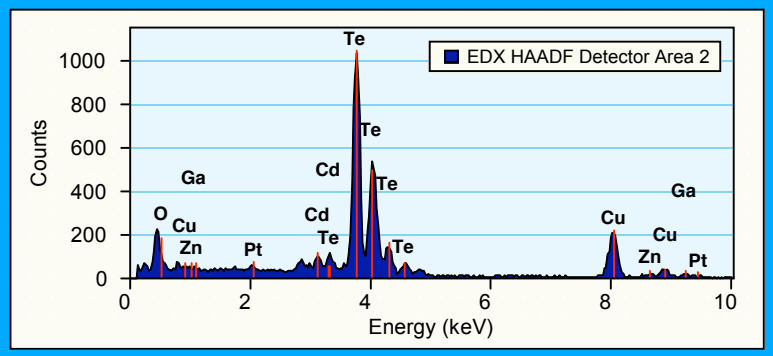


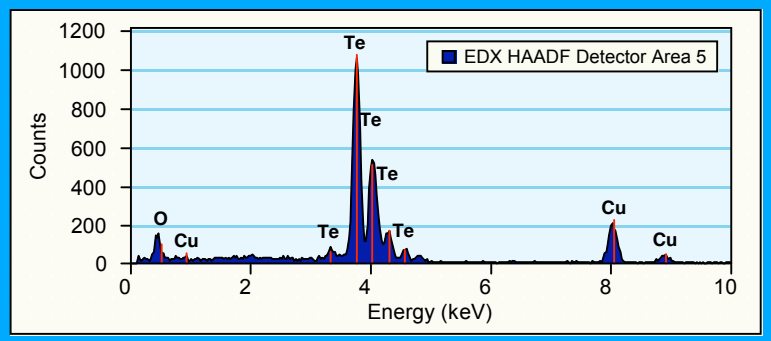


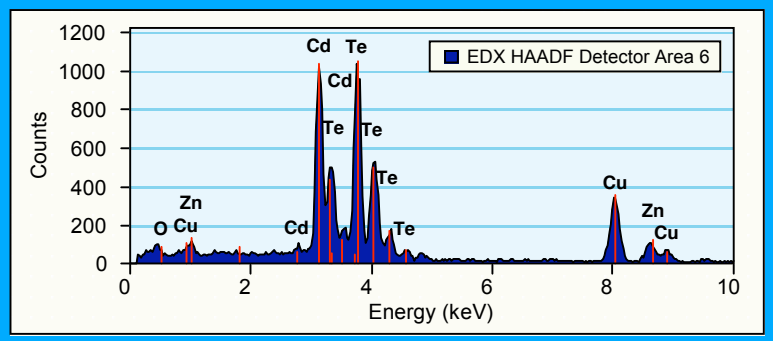
The Ga balls introduced during sample preparation of FIB







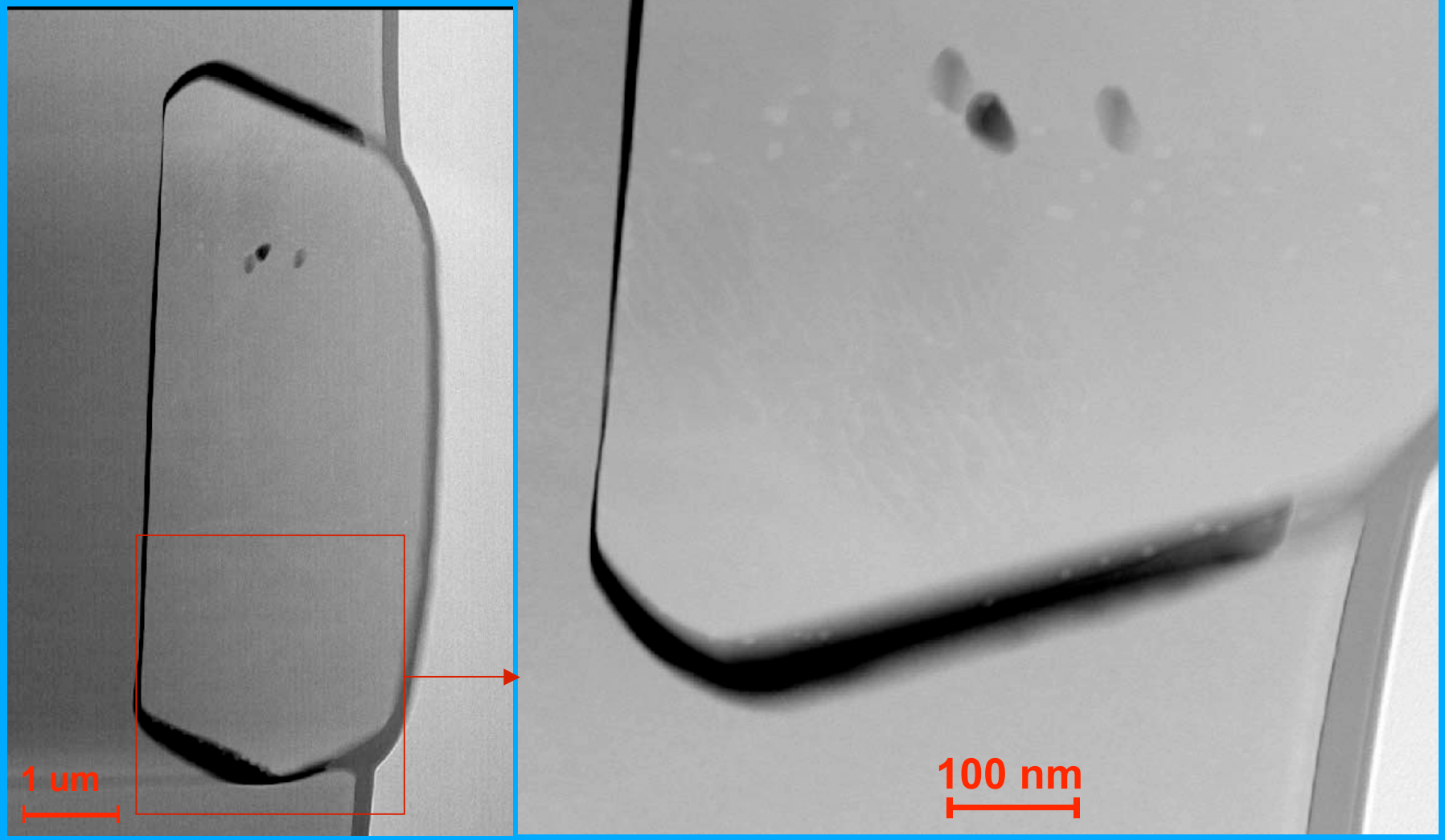




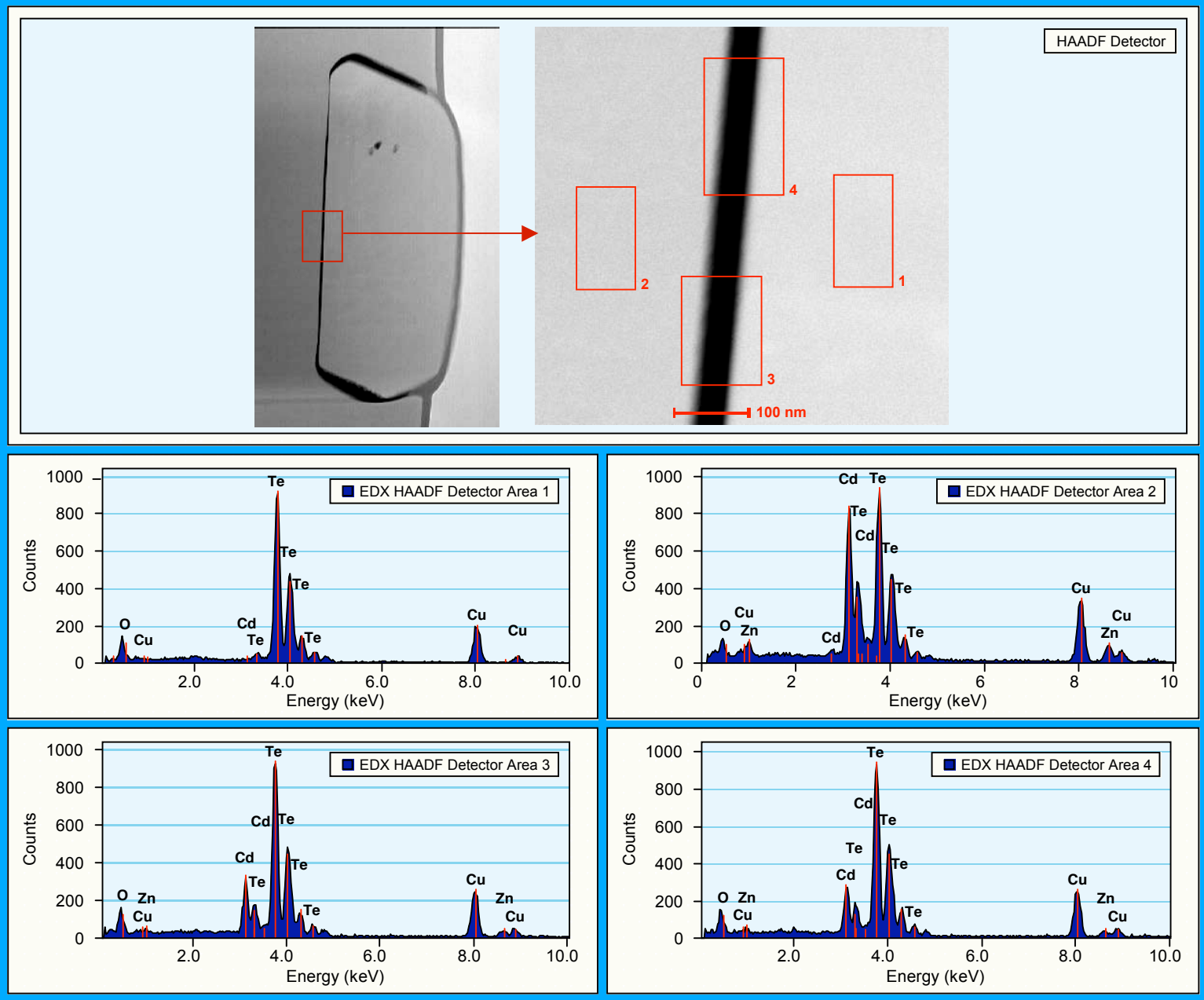
X-ray EDS analysis

Savannah River Project / Sample: CZT 3-7-8-3 (Side B Feature 2 / FIB section) / Tecnai G^2 / 07-12-2007 / LLNL

HAADF STEM image



Savannah River Project / Sample: CZT 3-7-8-3 (Side B Feature 2 / FIB section) / Tecnai G^2 / 07-12-2007 / LLNL



X-ray EDS analysis

Savannah River Project / Sample: CZT 3-7-8-3 (Side B Feature 2 / FIB section) / Tecnai G^2 / 07-12-2007 / LLNL